PB80-197346

A Study to Improve EPA Methods 15 and 16 for Reduced Sulfur Compounds

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Prepared for

Environmental Monitoring and Support Lab.
Research Triangle Park, NC

Apr 80

U.S. Department of Commerce
National Technical Information Service
NTIS

PB80-197346

United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Research Triangle Park NC 27711

EPA-600/4-80-023
April 1980

Research and Development

EPA

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A STUDY TO IMPROVE EPA METHODS 15 AND 16 FOR REDUCED SULFUR COMPOUNDS

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SwRI Project 01-4842-016
EPA Contract 68-02-2489

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

The following investigation was conducted at the request of the Office of Air Quality Planning and Standards. Test methods for the measurement of reduced sulfur compounds from stationary sources were evaluated. The work included studies of techniques and procedures for the gas chromatographic measurement of sulfur compounds commonly emitted from Kraft pulp mills and Claus sulfur recovery plants, permeation devices used as standards in those measurements, and the efficacy of compressed gas mixtures of sulfur compounds for use as quality assurance materials. Some information was also obtained on the comparative values of electrolytic conductivity and flame photometric detectors as devices for measuring reduced sulfur compounds.

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ABSTRACT

Equipment and procedures for the analysis of total reduced sulfur compounds according to EPA Methods 15 and 16 were studied.

A detector operating on the electrolytic conductivity principle was found to be equal or superior to the flame photometric detector for the analysis of H_2S, COS, CS_2, MeSH, DMS, and DMDS in the laboratory. Adsorption of these species on surfaces of the chromatographic system was found to be the main source of imprecision and inaccuracy in the analysis. Commercial samples of silica gel for analysis of H_2S and COS had to be given a pretreatment before they would provide the necessary separation. Glass and nickel tubing were used in the preparation of GC columns but were found to adsorb greater amounts of the sulfur compounds than FEP Teflon columns. Permeation devices containing the above sulfur compounds were found to permeate at uniform rates after one year of use, but observed rates did not agree well with vendor-certified rates in all cases. Aluminum cylinders containing mixtures of H_2S, COS and CS_2 and mixtures of H_2S, MeSH, DMS, and DMDS were periodically analyzed over four months. Results were erratic, and no firm conclusions as to stabilities of the mixtures could be drawn. The inherent inaccuracy of the chromatographic system used is likely to have been responsible for the data scatter.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

°C -- degree Celsius
EPA -- U.S. Environmental Protection Agency
ft -- foot
in -- inch
min -- minute
ng -- nanogram
ppm -- part per million
mL -- milliliter
m -- meter
mm -- millimeter

Symbols

H_2S -- hydrogen sulfide
COS -- carbonoxysulfide
CS_2 -- carbon disulfide
MeSH -- methane thiol
DMS -- dimethyl sulfide
DMDS -- dimethyl disulfide
FEP -- fluorinated ethylene propylene
ECD -- electrolytic conductivity detector
FPD -- flame photometric detector
N_2 -- nitrogen
TRS -- total reduced sulfur
GC -- gas chromatograph
ID -- inside diameter

SECTION 1

INTRODUCTION

This draft report concerns studies of EPA Methods 15 and 16, work performed in our laboratories as well as that reported in the recent literature. The goals were to gain intimate familiarity with the methods, in particular, and with the techniques of trace sulfur gas analysis, in general, and to perform specified studies designed to evaluate and perhaps improve the subject methods. Work Assignments specified that the following be studied:

1) The stabilities (variation of permeation rates with time) of permeation tubes containing hydrogen sulfide (H_2S), carbonoxysulfide (COS), carbon disulfide (CS_2), methane thiol (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS)

2) The stabilities (compatabilities) of bottled gas mixtures containing the above compounds in an inert gas

3) Interferences that may result from the presence of nonsulfurous substances

4) Methods for improving the dilution system

5) The performance of a conductivity detector as an alternative to the flame photometric detector (FPD)

6) The location of suitable sources for field testing of the methods.

In addition, several chromatographic systems developed in other laboratories are described. These include isothermal systems which allow the analysis of the four total reduced sulfur (TRS) compounds covered in Method 16 using a single instrument.

SECTION 2

CONCLUSIONS

At the time studies were begun, chromatographic equipment and conditions to be used were specified by the methods (Method 15 - Federal Register 41, pp. 43870-43873, October 4, 1976; Method 16 - Federal Register 41, pp. 42017-42020, September 24, 1976). Later, these regulations were modified (Method 15 - Federal Register 43, pp. 10866-10873, March 15, 1978; Method 16 - Federal Register 43, pp. 7568-7598, February 23, 1978) to allow other separation columns and conditions to be used provided they met certain criteria. Early laboratory investigations, then, were carried out using systems fabricated according to Section 12 of both methods. Instrumentation and equipment are described in Section 3, "Experimental".

The required flame photometric detector (FPD), while possessing the required sensitivity and selectivity, suffers from a nonlinear response and a limited dynamic range in the sulfur mode. Its signal is also affected (quenched) by the presence of non-sulfur-containing compounds which may coelute with the TRS compounds. A commercially-available detector operating on the electrolytic conductivity principle was evaluated in side-by-side laboratory tests and found to be equal or superior to the FPD with regard to sensitivity, selectivity and behavior toward certain interferences. Its response was essentially linear over the range of interest. This detector should at least be considered as an alternative to the FPD, that is, it is felt the FPD should not be specified as the detector to be used in the methods *a priori*.

A deactivated silica gel column for analysis of the Method 15 compounds (COS, H_2S and CS_2) was found to outperform all other columns tested provided that the substrate was pretreated with an acid wash. Commercial deactivated silica gel used "as received" was able to separate the materials of interest only at temperatures near ambient (25°C) and low carrier gas flow rates (20 mL/min). After a wash with concentrated hydrochloric acid, the same silica gel gave baseline separation of COS and H_2S at 55-60°C.

GC columns constructed of FEP Teflon tended to develop leaks with time due to the "cold flow" characteristic of the material. Columns constructed of glass and nickel tubing did not leak, but use of the metal column resulted in a partial loss of all Method 15 compounds. Compared to the Teflon column, the nickel column caused a loss of 15 percent of the COS, 65 percent of the H_2S and 17 percent of the CS_2. The glass column lost 21 percent of the H_2S. Thus, it appears that glass columns may be used in place of Teflon columns at a sacrifice in apparent sensitivity.

No isothermal separation of the four TRS compounds of Method 16 could be attained without the use of backflush techniques. Temperature programming allows this separation, but such a technique was determined to be unacceptable due to lengthy analysis time and leak problems caused by the "cold flow" of Teflon columns and fittings at elevated temperatures.

Several systems employing a backflush cycle have been found to perform the requisite Method 16 analysis in about ten minutes using a single instrument.

Permeation tubes of the O'Keeffe-type[1,2] containing H_2S, CS_2, MeSH, DMS and DMDS were found to permeate at a constant rate over a three-month period one year after date of purchase. The experimentally-determined rates were, in general, in fair agreement with those certified by the vendor.

A wafer-type device containing COS was also found to permeate uniformly after one year; however, its certified rate (790 ng/min) and observed rate (628 ng/min) did not agree. It is recommended that vendor-certified permeation rates be checked experimentally by the purchaser.

Aluminum cylinders containing low-ppm concentrations of COS, H_2S and CS_2 in N_2, and H_2S, MeSH, DMS and DMDS in N_2 were analyzed periodically over four months. A cylinder originally containing sub-ppm amounts of COS, H_2S, and CS_2 showed no COS or H_2S after two months, while the CS_2 remained constant. Cylinders originally containing greater than one ppm of COS, H_2S and CS_2 were essentially unchanged after four months.

Within the apparent accuracy of Method 16, analysis of cylinders containing the four subject gases did not vary over the test period. The use of these mixtures for in-the-field instrument calibration should be tested under rigorous field conditions.

All attempts to build a workable dilution system using the Komhyr A-150 pumps failed. When a back pressure of more than 1-2 cm Hg was encountered by the pump, it leaked at the pump head. The leak rate is sensitive to small changes in back pressure; therefore, dilution factors cannot be known with accuracy. A simple working dilution device was designed and shown to give precise results at ambient conditions with synthetic gas blends. This system is based on pressure-regulated flow through capillary tubing.

SECTION 3

EXPERIMENTAL

Gas Chromatographs:

Hewlett-Packard 5710A equipped with a Melpar Flame Photometric Detector (FPD), strip chart recorder, and A/D converter connected to a Hewlett-Packard Model 3354 Laboratory Data System. Attenuation range = 1X to 1024X.

Tracor Model 560 equipped with a Hall 700A Electrolytic Conductivity Detector (ECD), strip chart recorder and connected to the above-listed Hewlett-Packard integrator with an A/D converter.

Calibration system:

O'Keeffe-type[1,2] permeation tubes containing H_2S, CS_2, MeSH, DMS, and DMDS and a wafer-type device containing COS were purchased from Metronics, Inc., Palo Alto, California and were individually certified by the vendor.

Rate, Compound	Certified Permeation ng/min
H_2S	690 ± 2%
COS	790 ± 5%
CS_2	600 ± 2%
MeSH	380 ± 2%
DMS	520 ± 2%
DMDS	109 ± 5%

A Lauda Model B-1 water bath controlled at 30° ± 0.1°C kept the tubes at the temperature of their certification.

Once a week the tubes were removed from the tube chambers and weighed on a Mettler H51AR analytical balance with readability of 0.01 mg and precision (standard deviation) of ±0.01 mg. Tubes were handled using clean cotton gloves, and static charge was dissipated by brushing the tubes with a Staticmaster Brush, Model 1C200, Nuclear Products Company, El Monte, California.

Experimentally-observed permeation rates were obtained statistically as slopes of the linear regression line fitted to the weight versus time data assuming the first-order model

$$\mu_{y/x} = \beta_0 + \beta_1 X + \varepsilon$$

where $\mu_{y/x}$ = mean weight of permeation tube at time X
y = weight of permeation tube
X = time
β_0 = intercept
β_1 = slope (permeation rate)
ε = the increment by which any individual y may fall off the regression line.

The experimental permeation rate is defined as

$$\text{Permeation Rate (ng/min)} = b_1 \pm s_{b_1}\, t_{1-\alpha/2}\,(k-2)$$

where b_1 = estimated permeation rate, ng/min
k = number of data points
s_{b_1} = standard error of the estimated permeation rate b_1.
and $t_{1-\alpha/2}\,(k-2)$ = Student t with k-2 degrees of freedom at significance level α (two-sided test)

This is for a confidence interval of 100 (1-α)% For this study, α was chosen to be 0.05 to give a 95 percent confidence interval around the true average permeation rate.

Sample Valves: Teflon 6-port rotary valves, Model 50, were purchased from Rheodyne, Incorporated, Berkeley, California, and a 10-port sliding valve of unknown origin was provided by QAB.

Dilution System: All-Teflon system employing the recommended Komhyr A-150 pumps (Science Pump Corporation, Camden, New Jersey) and housed in an oven maintained at 120°C as specified in Sections 12.1.2 and 12.1.2.1.

GC Columns; Method 15:	Special silica gel was purchased from Tracor, Inc., Austin, Texas, and was gravity packed into 6-ft x 1/8-in sections of FEP tubing, glass tubing and nickel tubing. Some columns were prepared using silica gel which had been acid washed according to Thornsberry.[3] This was done by placing 10 g of the silica gel in a medium porosity fritted glass filter and washing with 30 mL of concentrated hydrochloric acid, 90 mL of distilled water, and 90 mL of acetone in that order. The flow rate was approximately 5-10 mL/min. After air drying, the substrate was packed into the column and conditioned overnight in the chromatograph at 150°C and 50-60 mL/min nitrogen carrier flow through the column.
GC Columns; Method 16:	A 36-ft x 1/8-in Stevens[4,5] column was prepared according to the method of Pecsar and Hartman.[6] This FEP Teflon column typically has a 9 percent (Wt/Wt) loading of a mixture composed of 96 percent polyphenyl ether PMPE-SR and 4 percent orthophosphoric acid on 40/60 mesh Teflon powder (Chromosorb T). This column separates H_2S, MeSH, and DMS. For the analysis of DMDS a 10-ft x 1/8-in FEP Teflon column filled with Chromosorb T was flow-coated with Triton X-305.

A commercial version of the Stevens column was later purchased from Supelco, Inc., Bellefonte, Pennsylvania.

Calibration gas cylinders were purchased from Scott Specialty Gases, Plumsteadville, Pennsylvania. The cylinders were Scott Aculife™ of treated aluminum.

Vendor analyses are as follows:

	Designation Cylinder	Compound	Concentration, ppm
Method 15	1A	COS	0.201
		H_2S	0.709
		CS_2	0.619
	2A	COS	1.02
		H_2S	2.36
		CS_2	1.54
	3A	COS	7.61
		H_2S	2.46
		CS_2	5.14
	4A	COS	2.69
		H_2S	11.1
		CS_2	6.14
Method 16	1B	H_2S	0.742
		MeSH	0.574
		DMS	0.619
		DMDS	0.866
	2B	H_2S	0.925
		MeSH	1.96
		DMS	1.93
		DMDS	1.38
	3B	H_2S	4.00
		MeSH	6.01
		DMS	4.76
		DMDS	2.83
	4B	H_2S	5.84
		MeSH	9.99
		DMS	7.39
		DMDS	5.52

Cylinder stability studies were performed using the originally-recommended columns and either an FPD or Hall 700A ECD for detection.

SECTION 4

RESULTS AND DISCUSSION

FLAME PHOTOMETRIC DETECTOR

The performance of the flame photometric detector of the Brody and Chaney design has been well documented.[6-12] Its main values lie in its high sensitivity and high selectivity toward sulfur compounds. It does have several troublesome disadvantages. A limited dynamic range forces careful selection of sample sizes and/or the use of a dilution system. For example, it was found that when a slow-eluting compound of ≃1 ppm and H_2S at ≃7 ppm were together in the same gas stream, a sample size that would allow the slow-eluting material to be quantitated at an attenuation of 1X would cause the H_2S peak to be off-scale at the least sensitive attentuation, 1024X.

It was suggested[13] that, in cases where actual emissions are found to be outside the ranges of concentrations used for instrument calibration, the substitution of a different size sample loop (either smaller or larger) could be used to bring the sample within range. By application of the square or square root, as appropriate, of the sample loop volume ratio to the results obtained with the substitute loop, the actual concentrations could then be calculated. This would, in theory, obviate the use of a dilution system to allow high concentrations to be quantitated. To test this theory, several concentrations of H_2S, COS, and CS_2 were generated and analyzed by Method 15 using two different sample loops of 2.1 mL and 0.6 mL. Log-log plots of peak area versus concentration (ppm) are shown in Figures 1-3. As an example, consider the case where a 10.0 ppm concentration of H_2S is analyzed using each of the two loops. With the smaller loop, an area of 3.5×10^5 area units is obtained. Assuming a quadratic response the calculated area for the 2.1-mL loop would be $(2.1/0.6)^2(3.5 \times 10^5) = 4.29 \times 10^6$ area units, corresponding to 13.5 ppm (35 percent high). The experimental area of the peak was found to be 2.9×10^6 area units. Even larger errors result when this method is applied to COS (55 percent high) and CS_2 (95 percent high). The point is clear; assumption of a quadratic response of the FPD to these compounds may lead to large errors.

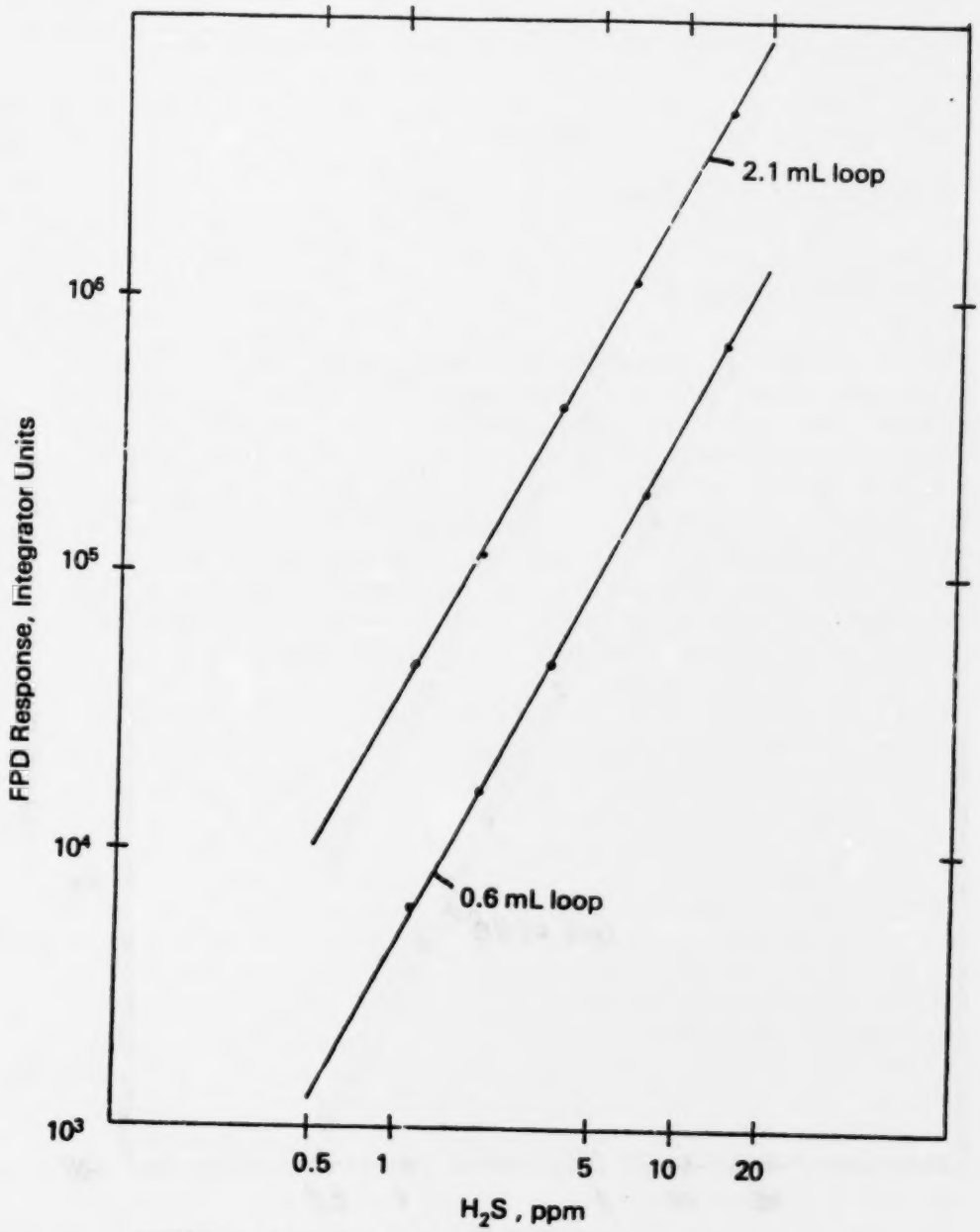

FIGURE 1. H_2S CALIBRATION CURVES AT TWO VOLUMES

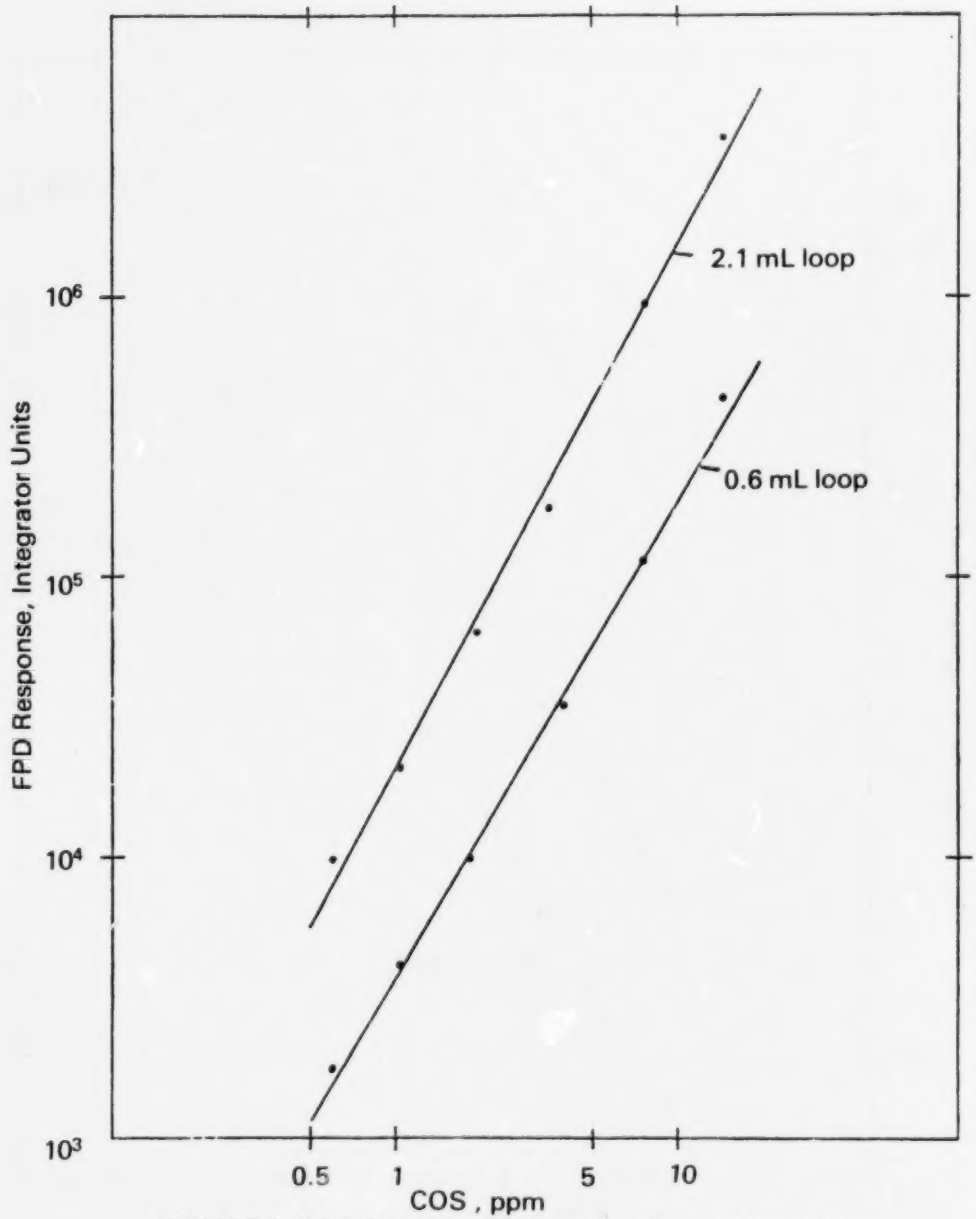

FIGURE 2. COS CALIBRATION CURVES AT TWO VOLUMES

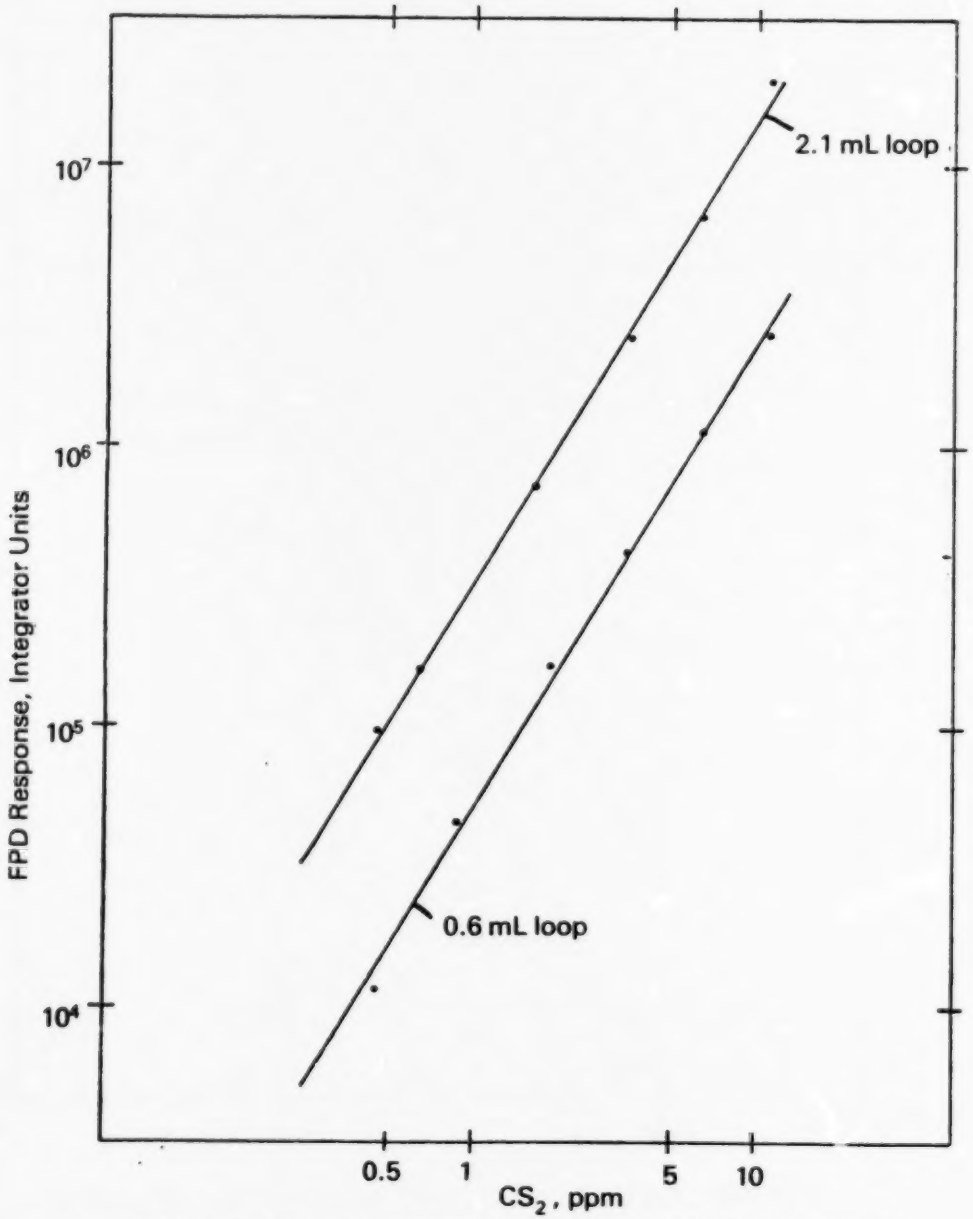

FIGURE 3. CS_2 CALIBRATION CURVES AT TWO VOLUMES

Nonlinearity of response and varying responses to different sulfur-containing species are drawbacks that must be recognized when using the FPD.

The nonlinearity of response of the FPD toward sulfur-containing species is sometimes treated by use of a "linearizer" which takes the square root of the signal. Extrapolations of calibration lines generated with such a device may result in large errors (up to 400 percent) being incorporated in the measurement.[14]

Greer and Bydalek[10] characterized the response of the Melpar FPD for H_2S and SO_2 and concluded that it could be defined by the general equation

$$R = k_1 k_2 K S^2 10^{-\alpha K S^2}$$

where K = equilibrium constant for the reaction $S + S \rightleftharpoons S^2$
S and S^2 = masses of their respective materials in the flame
k_1, k_2 and α = constants which may be determined experimentally.

They state that the most simple theoretically sound calibration curve is a log-log plot of detector response versus sulfur mass. This gives a straight line with a slope of 2 up to the point of self-absorption, corresponding to a range of 0 to about 100 ng of sulfur. Other workers have shown that a plot of response versus sulfur compound concentration is linear up to 1 ppm, at which point a negative deviation is observed.[5]

Regression lines were calculated for the plot of peak area versus log concentration (ppm) for H_2S, COS and CS_2 over the entire range which could be conveniently generated with the described permeation tube system. The data appear in Tables 1-3. Assuming the simple relationship $A = K[S]^n$ to hold, where A = peak area and [S] = sulfur gas concentration in ppm, values for the exponent n and the proportionality constants K were determined for each compound using this equation in logarithmic form. From $\log A = \log K + n \log [S]$, n was obtained as the slope of the linear regression line fitted to the log area versus log [S] data for each compound. Duplicate or triplicate analyses of each concentration of each sulfur compound were used to determine the regression lines. For COS, n = 1.77 with a correlation coefficient of 0.995. For H_2S and CS_2, the fits were similar with n = 1.74 (correlation coefficient of 0.995) and 1.72 (correlation coefficient of 0.997), respectively. These values were obtained over a limited range, however, and attempts to use the values outside this range would not be advised.

In general, we found that the actual shape of experimental log-log calibration lines was slightly curvilinear upward (see Figures

TABLE 1. FPD RESPONSE TO H_2S CONCENTRATION

[H_2S], ppm	Log [H_2S]	Peak Area	Log Area
0.6	-0.22185	36943	4.56753
"	"	34881	4.56259
1.0	0.00000	78906	4.89711
"	"	77666	4.89023
2.0	0.30103	245568	5.39017
"	"	247294	5.39321
3.0	0.47712	480303	5.68152
"	"	490872	5.69097
4.0	0.60206	810502	5.90875
"	"	833298	5.92080
5.0	0.69897	1706374	6.23207
"	"	1711639	6.23341

Slope = 1.74
Intercept = 4.91
Correlation Coefficient = 0.995

TABLE 2. FPD RESPONSE TO COS CONCENTRATION

[COS], ppm	Log [COS]	Peak Area	Log Area
0.6	-0.22185	27271	4.43570
"	"	25583	4.40795
0.9	-0.04576	54150	4.73360
"	"	53481	4.72820
1.9	0.27875	161630	5.20852
"	"	163584	5.21374
2.7	0.43136	340092	5.53160
"	"	341852	5.53384
3.7	0.56820	564883	5.75196
"	"	564333	5.75154
4.7	0.67210	1181471	6.07242
"	"	1189395	6.07523

Slope = 1.77
Intercept = 4.79
Correlation Coefficient = 0.995

TABLE 3. FPD RESPONSE TO CS_2 CONCENTRATION

$[CS_2]$, ppm	Log $[CS_2]$	Peak Area	Log Area
0.35	-0.45593	33948	4.53081
"	"	34858	4.54230
"	"	35230	4.54269
0.55	-0.25964	83608	4.92225
"	"	82768	4.91786
"	"	80509	4.90584
1.1	0.04139	265116	5.42344
"	"	271437	5.43367
"	"	275103	5.43950
1.6	0.20412	474967	5.67666
"	"	488780	5.68911
"	"	486569	5.68714
2.3	0.36173	767023	5.88481
"	"	781205	5.89277
"	"	799125	5.90261
3.0	0.47712	1750687	6.24321
"	"	1752852	6.24375

Slope = 1.72
Intercept = 5.34
Correlation Coefficient = 0.997

2 and 3) with increasing concentration. This can be explained by the observation that varying amounts of the TRS compounds are adsorbed by the chromatographic system, mainly the column, packing and detector. It has been reported[6] that detector response to H_2S was reduced by an order of magnitude when a five-foot section of empty 1/8-in Teflon tubing was placed between the sample valve and the GC column. If the amount adsorbed is relatively constant, it follows that the initial fraction adsorbed becomes increasingly greater as the concentration decreases.

This loss of TRS compounds (in particular H_2S) is the main contributor to inaccuracy and imprecision in the two methods. It is necessary to passivate a fresh system (the sample loop, column, detector and connecting tubing) by repeated injections of sample gas or by several injections of a more concentrated mixture of a sulfur gas or gases. While this is necessary to attain reasonable repeatability, its effect is not lasting, and repassivation is required after a few hours. This observation is consistent with an adsorption-desorption mechanism in which sites in the system are rapidly tied up by reactive sulfur species, and then in a much slower process, reactivation occurs, presumably due to the sweeping action of the carrier gas.

Loss of reactive materials during attempted analysis of trace amounts is well known and can be a major problem to the chromatographer. In the methods studied, several precautions should be taken to minimize quantitation errors introduced by the adsorption-desorption phenomenon. First, use of stainless steel in contact with the sample is to be avoided. Some workers[15] have used stainless steel tubing for GC columns in the analysis of sulfur gases in hydrocarbon streams, but concentration levels were slightly higher and losses from long sample lines were not a problem in this case. Substitution of Teflon components is not a panacea, for the "cold flow" characteristics of the polymer may cause leaks (vide supra). The current studies were carried out with Teflon rotary six-port valves which had an upper temperature limit of 60°C, according to the manufacturer. Even at ambient temperature, periodic tightening of the valve fittings was required to stop leaks. Conversations with representatives of the kraft paper industries in the U.S. and in Canada revealed that sample valves of Carpenter 20 and, more recently, Hastalloy C are used in the analysis of low levels of TRS compounds with entirely satisfactory results. A representative of Valco, Inc. (Houston, Texas), a major supplier of valves for gas and liquid chromatography, claims that rotary valves of Hastalloy C are in widespread use by the petroleum industry for the ppm and sub-ppm analysis of sulfur gases. Such valves are claimed to be as "inert" as Teflon but have a much higher temperature limit and no leak problems.

Some FPD detectors may be modified to reduce sample losses. A stainless steel jet was supplied with the Melpar FPD in our Hewlett-Packard GC. When the metal jet was replaced with a glass jet (purchased from Tracor Instruments and supplied with the Melpar FPD in their chromatographs), peak growth was minimized. Figures 4-6 illustrate the improvement realized.

Although not tested, it is conceivable that the presence of a low level of, say, H_2S in the carrier gas would continually passivate the system at a small loss in dynamic range due to background. This low level could be generated by passing the carrier gas over a low-rate permeation tube.

Greatest precision would be obtained when samples and calibration gases of the same approximate concentrations are injected at even intervals under steady chromatographic conditions. A continuous GC monitor with a relatively fast analysis time (≈10 min) would appear to be the most reasonable way to maximize both precision and accuracy in the analysis of the subject compounds at the low-ppm level.

HALL 700A ELECTROLYTIC CONDUCTIVITY DETECTOR

A detector capable of being operated in a sulfur-specific mode was used in these laboratories in side-by-side comparisons with the FPD. This detector, the Hall 700A Electrolytic Conductivity Detector, was found to be the equal of the FPD with respect to sensitivity and superior in its independence from response quenching by the presence of hydrocarbons. In addition, its response was found to be linear over the range of concentrations of COS, H_2S and CS_2 generable with the available permeation tubes (typical calibration curves shown in Figure 7 with calibration data listed in Tables 4, 5 and 6). Compare the responses of the FPD and the Hall ECD to varying amounts of the sulfur compounds of Method 15. Conditions are listed in Table 7 and the chromatograms shown in Figure 8. Traces 1 and 2 show the abrupt change in peak size which occurs with the FPD detector when the sample masses are reduced by 72 percent. Traces 3 and 4 show the more nearly linear response of the Hall ECD under the same conditions and display the excellent peak shapes attained.

In the sulfur mode, the Hall detector converts sulfur-containing species to SO_2 by air oxidation in a heated nickel tube reactor at 750-1000°C. The reactor effluent is scrubbed and passed into the conductivity cell containing a flow of methanol (0.5-0.7 mL/min) as electrolyte. The conductivity change is measured, and the electrolyte is passed through an ion exchange cartridge containing 50 percent

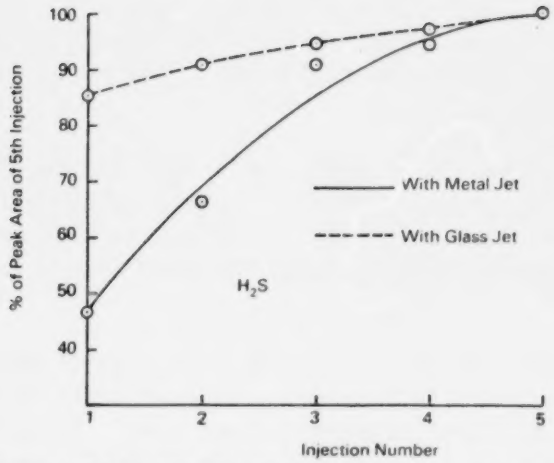

FIGURE 4. H_2S PEAK GROWTH WITH GLASS AND WITH METAL FPD JETS

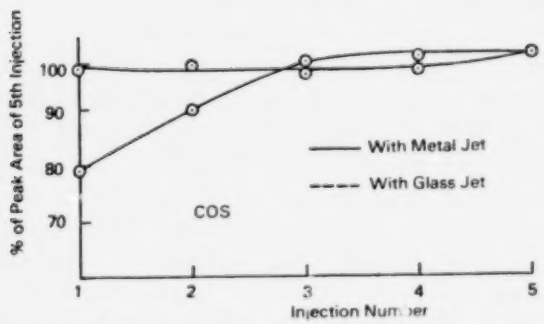

FIGURE 5. COS PEAK GROWTH WITH GLASS AND WITH METAL FPD JETS

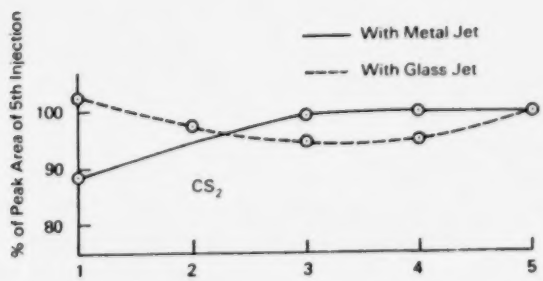

FIGURE 6. CS_2 PEAK GROWTH WITH GLASS AND WITH METAL FPD JETS

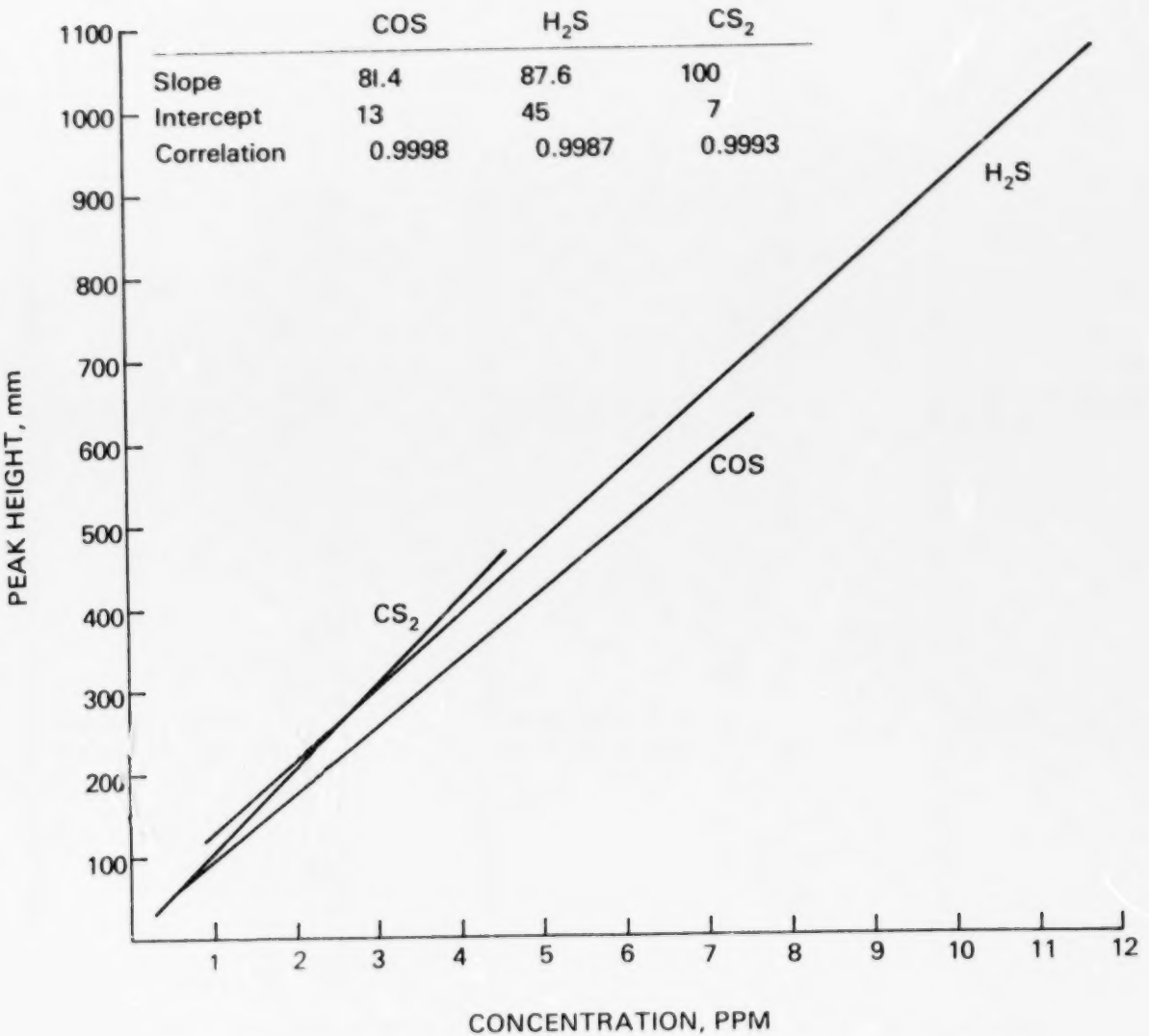

FIGURE 7. TYPICAL CALIBRATION CURVES WITH HALL 700A ECD

TABLE 4. HALL 700A ECD RESPONSE TO COS CONCENTRATION

[COS], ppm	Peak Height, mm
0.5	49
0.6	61
0.9	91
1.2	115
2.0	172
3.5	297
7.6	632

TABLE 5. HALL 700A ECD RESPONSE TO H_2S CONCENTRATION

[H_2S], ppm	Peak Height, mm
0.9	100
1.0	121
1.2	170
2.0	227
3.0	329
5.8	538
11.8	1080

TABLE 6. HALL 700A ECD RESPONSE TO CS_2 CONCENTRATION

[CS_2], ppm	Peak Height, mm
0.3	34
0.4	42
0.5	59
0.8	82
1.1	128
2.1	220
4.6	465

TABLE 7. COMPARISON OF FPD AND HALL 700A ECD RESPONSES

Compound	Concentration, ppm	ng S in 2.1 mL	ng S in 0.6 mL
COS	3.1	8.52	2.43
H_2S	4.8	13.19	3.77
CS_2	1.8	9.89	2.83

Column: 6-ft x 1/8-in FEP Teflon filled with acid-washed, deactivated silica gel.
Oven temperature: 50°C
Carrier gas: N_2 at 20 mL/min
Recorder Speed: 0.5 in/min

Results

Compound	Peak Heights (mm) of 2.1 mL sample		Peak Heights (mm) of 0.6 mL sample	
	FPD	Hall ECD	FPD	Hall ECD
COS	47.5	144.5	5.5	60
H_2S	216.5	218.0	20.5	85
CS_2	75.0	119.0	7.5	39

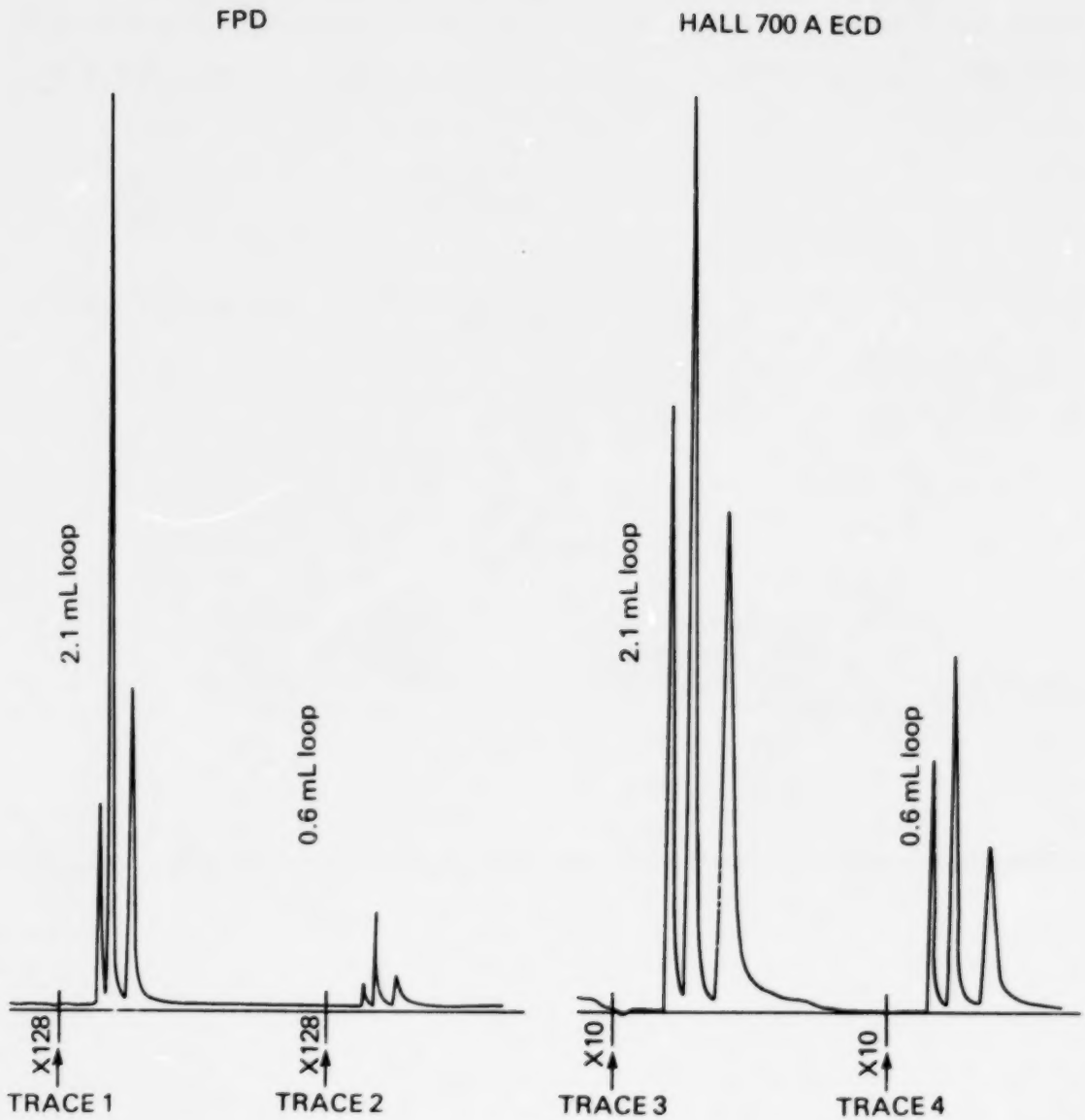

FIGURE 8. FPD AND HALL 700A ECD RESPONSES

IRN-77 and 50 percent IRN-150 and is then recycled to the cell. A diagram of the reactor appears as Figure 9.

Tracor claims no interferences result from the coelution of hydrocarbons with sulfur compounds. Some maintenance is required by the Hall ECD, because the electrolyte reservoir must be periodically topped up and the ion exchange column replaced from time to time. These chores are minor; however, it was necessary to replace the nickel reactor tube on our test instrument, a job requiring several hours of downtime.

It is felt that the Hall ECD should be strongly considered as an alternative detector in Methods 15 and 16 and that a field test comparing it to the FPD is called for.

COLUMNS AND SYSTEMS

All column materials evaluated in this study were packed in 1/8-in (3.175 mm) FEP Teflon tubing. To test the effect of replacing the Teflon by other "inert" materials, three 2-m x 2-mm ID columns, one FEP Teflon, one glass, and one nickel, were filled with acid-washed Tracor Special Silica Gel and used for the analysis of a permeation tube-generated blend of H_2S (0.90 ppm), COS (0.48 ppm) and CS_2 (0.35 ppm). A sample loop volume of 2.1 mL determined that the masses of the sulfur compounds were 2.6, 2.5, and 2.3 ng per injection, for H_2S, COS, and CS_2, respectively.

Each column was "passivated" by repeated injections of the gas blend, six replicate analyses were performed, and the average peak areas were calculated. As can be seen in Figure 10, the appearances of the chromatograms obtained with the Teflon and glass columns are similar. Some loss of COS and H_2S is observed with the glass column with peak areas of 75 percent and 79 percent, respectively, of the Teflon column results. The CS_2 peak was higher, and its integration was 109 percent of the Teflon column results. This latter result may be an artifact of the differing peak shapes obtained on the glass column. Peak retention times obtained on the nickel column were essentially identical to those of the Teflon, but some loss of all compounds was observed with the nickel column. Only 35 percent of the H_2S, 85 percent of the COS, and 83 percent of the CS_2 peak areas (relative to the Teflon column) were observed. These results do not necessarily rule out the use of nickel tubing for the columns, for losses on the column depend upon concentration or at least upon mass flux of sulfur-containing material. However, if losses in the sample line are appreciable, then the added losses on the column and the nonlinearity of the FPD detector may, in combination, reduce the apparent sensitivity of the method(s) to an unacceptable level.

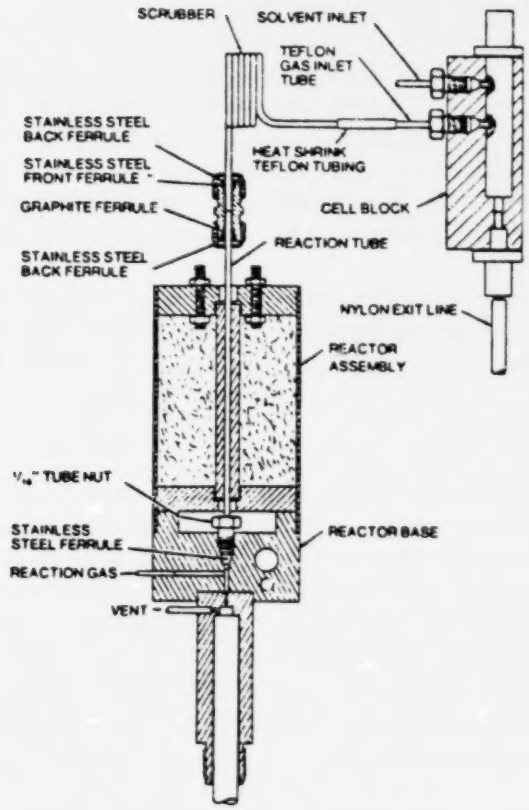

FIGURE 9. HALL 700A ECD REACTOR-CONDUCTIVITY CELL (SULFUR AND NITROGEN MODES)

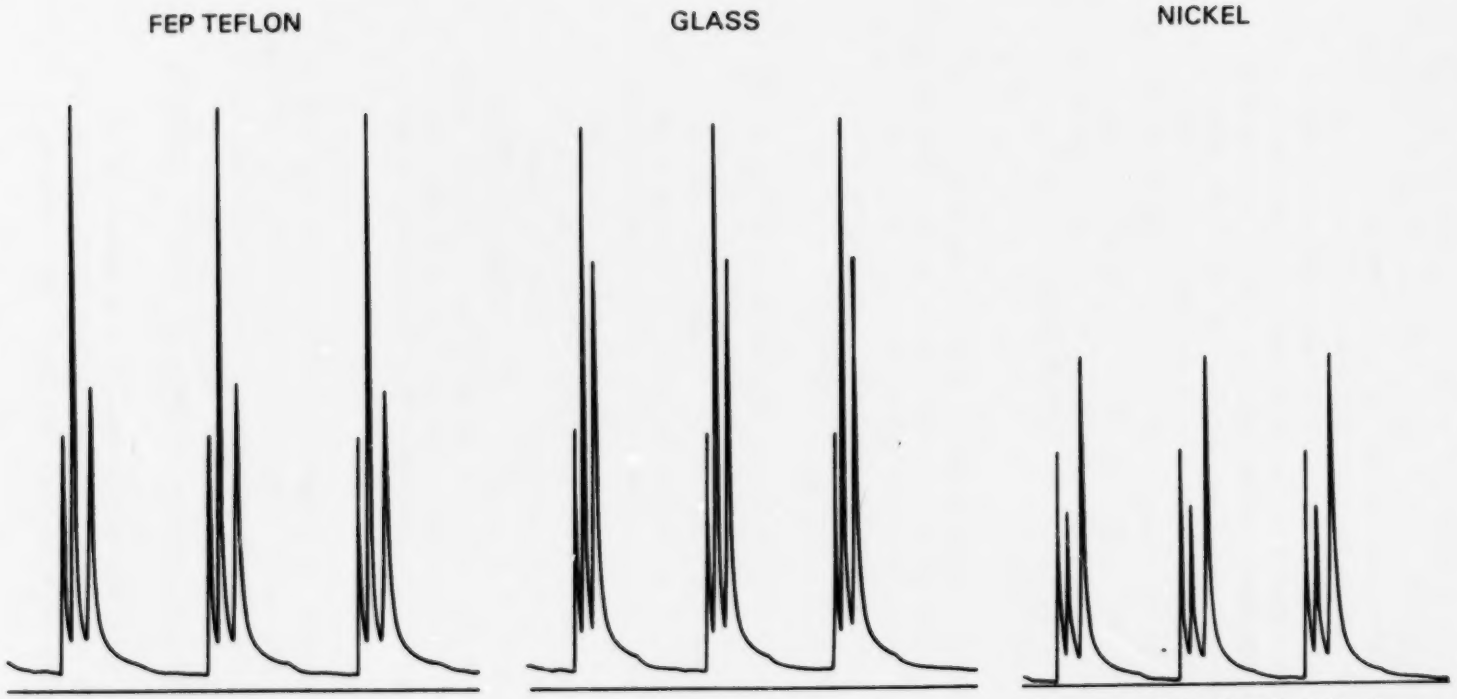

FIGURE 10. EFFECT OF TUBING MATERIAL ON PEAK SHAPES

The recommended silica gel column was prepared using Tracor Special Silica Gel. Deactigel,® a deactivated silica gel appearing in Catalog 22 of Applied Science Laboratories, Inc., State College, Pennsylvania, could not be purchased. A sales representative said the material had been withdrawn from the market because batch-to-batch performance was erratic. Two samples of the Tracor material were obtained, and columns constructed from the substrate "as received" were unable to separate COS and H_2S at temperatures above ambient (25°C). The effect of this is clear; such a column could not be used in the field during warm weather conditions except when housed in a cryogenic container. However, if the silica gel was acid-washed with concentrated hydrochloric acid and then with water, it was capable of baseline separation of COS and H_2S at 50°C or slightly above[3] (see Section 3, "Experimental"). A deactivated silica for this analysis is offered commercially by Supelco, Inc. but was not evaluated.

To determine the possible interference of CO_2 in a Method 15 analysis, a dilution gas mixture of 10 percent CO_2 in N_2 was substituted for the nitrogen flow over the permeation tubes, and low levels (1-2 ppm) of COS, H_2S, and CS_2 were generated and analyzed. Using the silica gel column, no interference by CO_2 was observed.

Separation of the subject compounds could also be effected with a 14-in x 1/8-in Teflon column filled with Chromosorb 102. To achieve a reasonable analysis time and CS_2 peak shape, it was necessary to use a temperature program. With a program of 45°C (2 min hold) to 130°C at 32°/min (2 min hold), the following retention times were obtained: H_2S - 0.95 min; COS - 1.44 min; and CS_2 - 4.90 min. The necessity to use a temperature program would seem to speak against the use of this column for two reasons. First, reproducible retention times are difficult to obtain. This in turn affects peak shape and introduces errors if peak heights are being used for quantitation. Second, leaks at the points of column attachment were a frequent problem and could be attributed to "cold flow" of the thermoplastic Teflon tubing at elevated temperatures.

A specially-treated Porapak QS column[16] also separated the Method 15 compounds, but it, too, had to be temperature programmed and suffered from the same drawbacks as the Chromosorb 102 column. According to de Souza, et al.,[16] this column is capable of separating H_2S, COS, SO_2, MeSH, DMS, and DMDS using a temperature program from 30° to 210°C.

Our conclusion, based upon the above results and others (vide infra), is that the example silica gel column is the column of choice for Method 15 but may require an acid wash to obtain the required performance.

The above-mentioned Porapak QS column (available from Supelco as Supelpak-S) was found to separate the TRS compounds of Method 16, but again, it is necessary to use a temperature program. In our instrument, the baseline would drift off scale at low attenuation when the upper temperatures of the program were reached. Attempts to correct this failed, and a factory representative could offer no solution.

The Stevens[4,5] polyphenyl ether/H_3PO_4 column was prepared according to the method of Pecsar and Hartman.[6] Resolution of H_2S, MeSH, and DMS was excellent, and in fact a 12-foot section could be used to resolve all four TRS materials. Because of the broad shape of the DMDS peak, <1 ppm concentrations of this relatively nonvolatile compound could not be observed.

Neither this column nor a similar, commercially-prepared column could separate COS and H_2S. This fact alone could disqualify its use, for it has been reported by de Souza[17] and others[18] that COS has been found in recovery boiler stacks and lime kilns. COS is nonodoriferous and is not a TRS compound. If not separated, its presence could erroneously show a process to be out of compliance.

When 10 percent CO_2 was added to a low-level (0.5-2 ppm) synthetic blend of the four TRS compounds, no change in the analysis occurred compared to those without CO_2.

At least four systems are known which can be used to analyze for TRS compounds isothermally and with a single injection on a single instrument. They have been reported by de Souza[17] of the Pulp and Paper Research Institute of Canada and by Jain[19] of the National Council of the Paper Industry for Air and Stream Improvement, Inc. A continuous monitor offered by Bendix Environmental and Process Instruments and one under development by Tracor make the same claims. It was beyond the scope of the program to evaluate these systems in the laboratory. From information that is available, all systems obviate the need for two chromatographs to perform Method 16. The Tracor system does not separate MeSH, DMS, and DMDS but quantitates them together using a linearized FPD. The de Souza Automatic GC Monitor quantitates H_2S, COS, SO_2, MeSH, DMS, DMDS, and TRS using three columns in three different ovens. The Bendix analyzer claims to separate all TRS compounds from COS and to have a superior sample-handling system. Again, it is felt that a continuous-type analyzer would be best from the standpoints of accuracy and precision.

PERMEATION TUBE STUDY

Time required to reach permeation rate equilibrium after a temperature

change and the long-term rate stabilities of a number of O'Keeffe-type permeation tubes have been investigated by Williams.[20] Compounds studied included H_2S, MeSH, and DMS. He concluded that rates for MeSH and DMS were stable within one percent over periods from 7-17 days. H_2S permeation rates decreased by three percent over 20 days, but insufficient data were available to predict a continued decrease. A personal communication with the author revealed that no further studies had been carried out.

Our three-month study of permeation tubes containing each of the Method 15 and Method 16 compounds showed the rates to remain unchanged (within two percent) over the entire period (Figures 11-16). Of interest is the fact that the experimentally-determined rates agreed well with the vendor-certified rates in three cases (CS_2, H_2S, and DMS), fairly well in one (MeSH) and poorly in two others (COS and DMDS). The comparison of rates is given in Table 8.

Experimentally determined values were low in all cases, ranging from 99.8 percent to 79.5 percent of the certified rates. The uniformly low nature of the results is likely due to a small temperature difference between the baths in which the two sets of determinations were made, but a temperature difference does not explain the range of discrepancies found. Since the rates were determined after approximately one year of use, it cannot be stated that the certified rates were in error. However, we feel that it would be prudent for purchasers of tubes to verify experimentally their permeation rates.

GAS CYLINDER STABILITY STUDIES

Table 9 contains the vendor analyses and our periodic analyses of the four cylinders (1A-4A) containing Method 15 compounds. The same information for the four cylinders containing the Method 16 compounds is given in Table 10. Immediately apparent is the fact that several of the mixtures contained one or more components in a concentration too high to be conveniently analyzed with our available permeation tube system. The reason given by the supplier for the high values was that it was necessary to make blends of concentrations higher than those specified so that the inevitable loss of some of the reactive materials (on the inner walls or by reaction) could be allowed for. If the amount of the loss was underestimated, a high value resulted. Rather than return the cylinders, it was decided to begin the stability study with the materials as received.

Tables 9 and 10 reveal a considerable amount of scatter in the data. This is attributed to the inherent lack of precision and accuracy

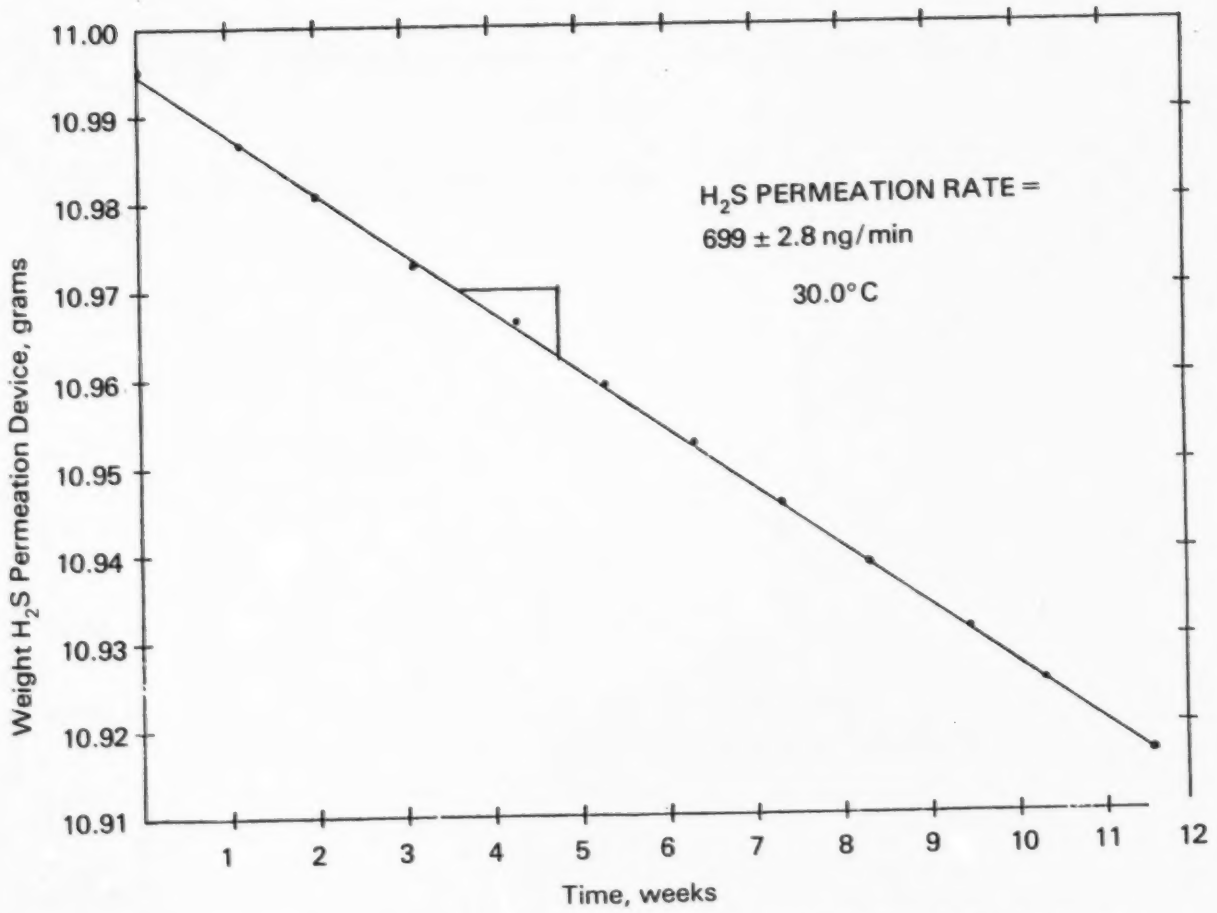

FIGURE 11. GRAVIMETRIC CALIBRATION OF H_2S PERMEATION DEVICE

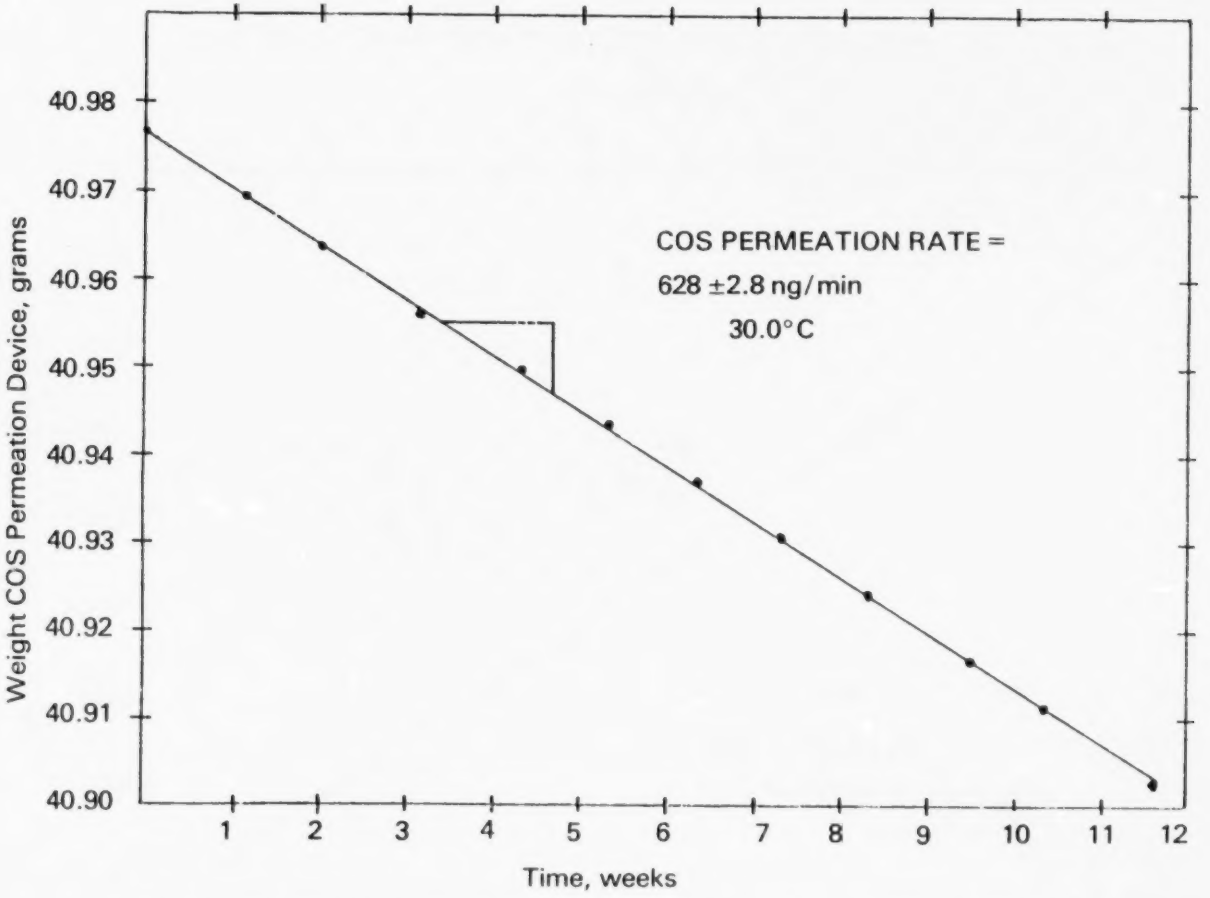

FIGURE 12. GRAVIMETRIC CALIBRATION OF COS PERMEATION DEVICE

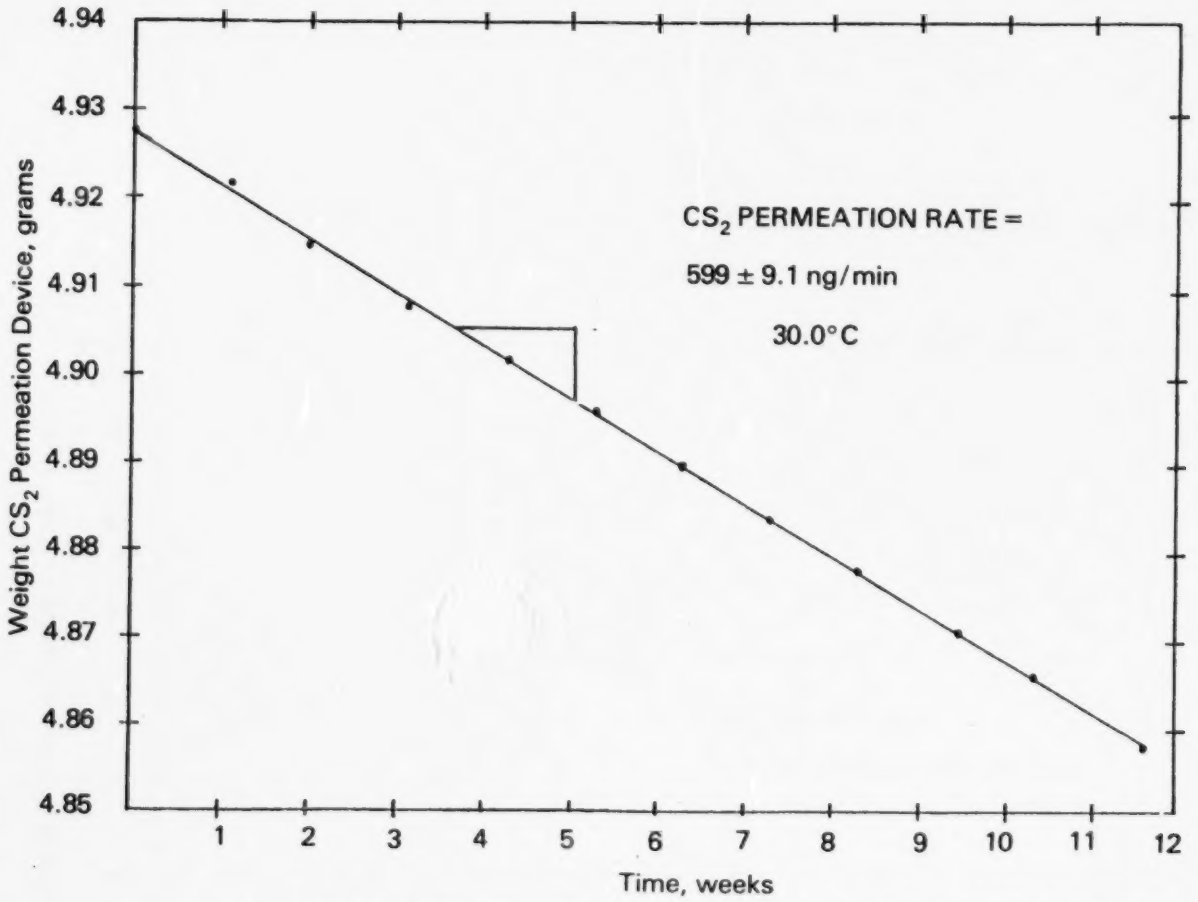

FIGURE 13. GRAVIMETRIC CALIBRATION OF CS_2 PERMEATION DEVICE

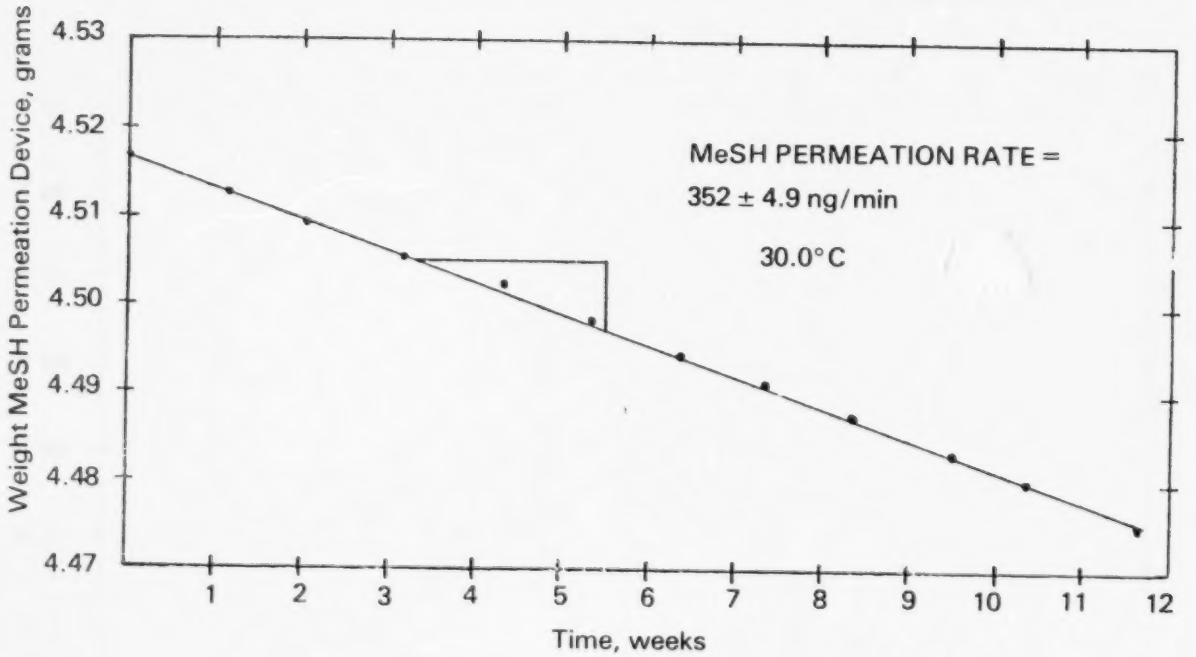

FIGURE 14. GRAVIMETRIC CALIBRATION OF MeSH PERMEATION DEVICE

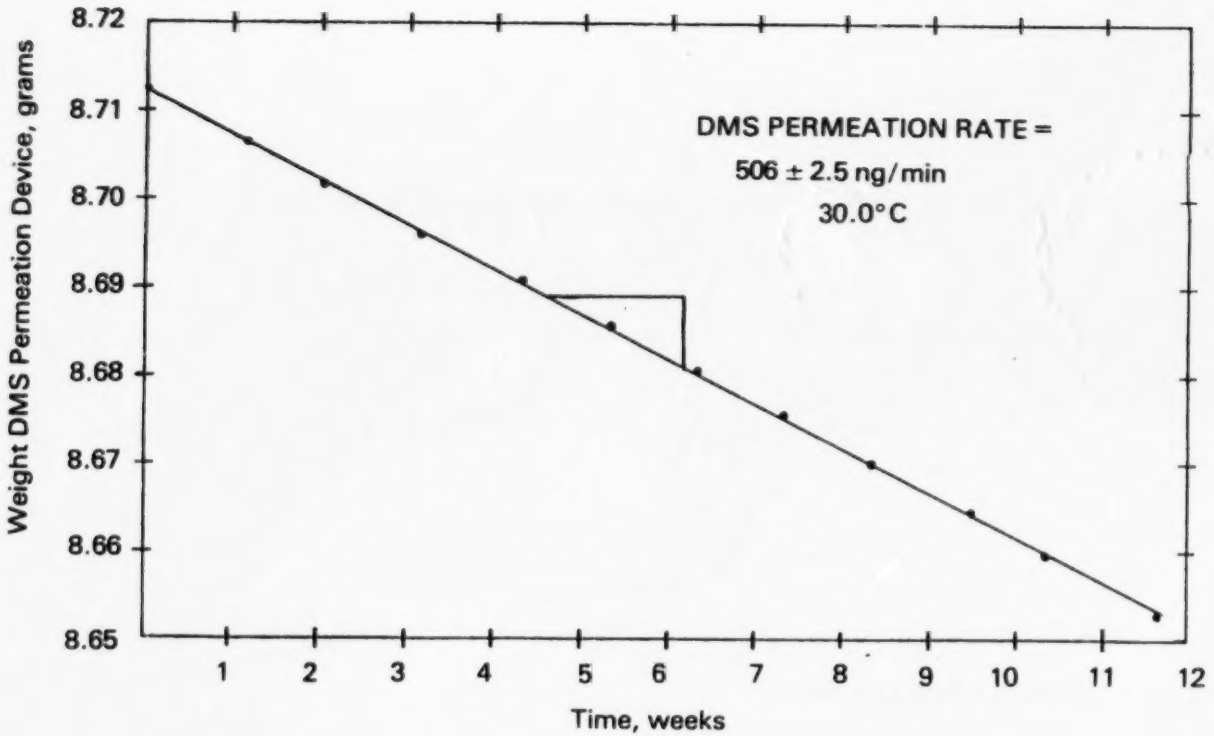

FIGURE 15. GRAVIMETRIC CALIBRATION OF DMS PERMEATION DEVICE

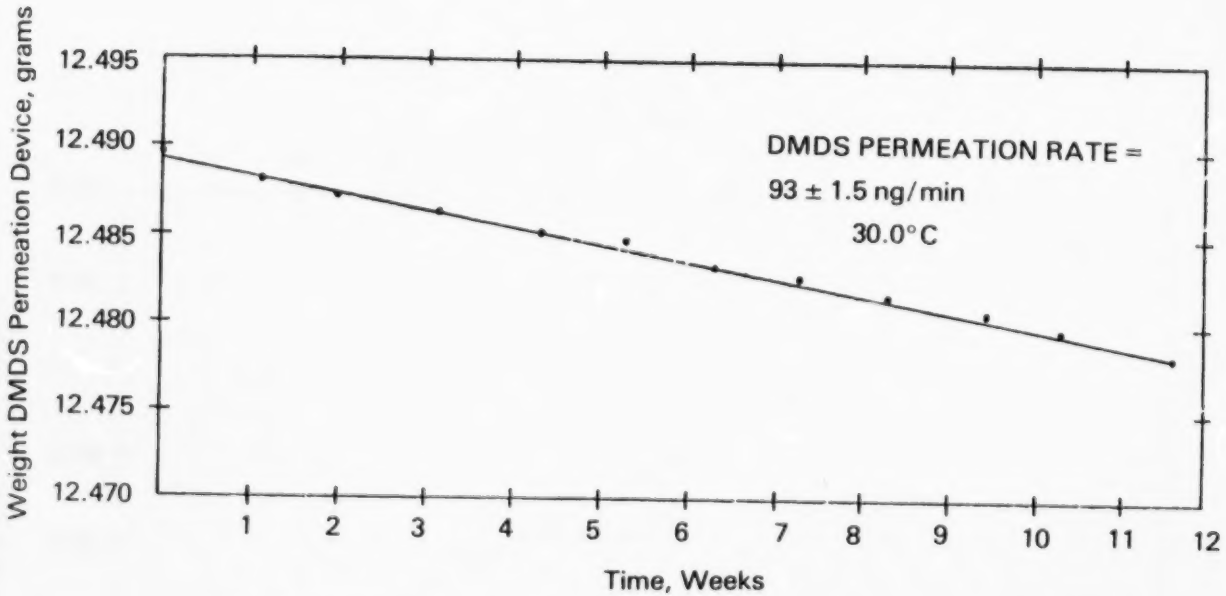

FIGURE 16. GRAVIMETRIC CALIBRATION OF DMDS PERMEATION DEVICE

TABLE 8. COMPARISON OF EXPERIMENTALLY-DETERMINED AND VENDOR-CERTIFIED PERMEATION RATES

Compound	Certified Rate	Experimental Rate	% of Certified Value	Δ%
H_2S	690±2%	669±0.4%	97.0	- 3.0
COS	790±5%	628±0.5%	79.5	-20.5
CS_2	600±2%	599±1.5%	99.8	- 0.2
MeSH	380±2%	352±1.4%	92.6	- 7.4
DMS	520±2%	506±0.5%	97.3	- 2.7
DMDS	109±5%	93±1.6%	85.3	-14.7
				$\overline{\Delta\%}$ = - 8.1%

TABLE 9. GAS CYLINDER STABILITY STUDY - METHOD 15

Cylinder Designation	Compound	Date of Analysis (Conc. in ppm)					
		12-15-79[a]	1-26-79	3-7-79	3-16-79	4-10-79	5-11-79
1A	COS	0.201	0.0	0.0[b]	0.0	0.0	0.0
	H_2S	0.709	0.4	<0.1[b]	0.10		0.15
	CS_2	0.619	0.7	0.55	0.65	0.82	0.64
2A	COS	1.02	1.0	0.70	0.67	0.62	0.59
	H_2S	2.36	2.1	1.90	2.25	2.95	2.67
	CS_2	1.54	1.9	1.55	1.75	1.90	1.58
3A	COS	7.61	3.2	3.56	3.95	3.85	4.25
	H_2S	2.46	3.8	4.20	4.85	5.90	6.62
	CS_2	5.14	7[b]	6.1[b]	6.4[b]	7[b]	6[b]
4A	COS	2.69	1.30	c	c	c	c
	H_2S	11.1	9.1	c	c	c	c
	CS_2	6.14	9[b]	c	c	c	c

a. Final vendor analysis before shipping
b. Outside calibration range - values obtained by extrapolation
c. Contents of cylinder lost by leak at valve

TABLE 10. GAS CYLINDER STABILITY STUDY - METHOD 16

Cylinder Designation	Compound	Date of Analysis (Conc. in ppm) 12-15-78[a]	1-30-79	2-28-79	3-12-79	3-28-79	5-15-79	6-4-79
1B	H_2S	0.742	0.20	0.20	<0.1[b]		0.15[b]	<0.1[b]
	MeSH	0.574	0.75	0.68	0.25		0.77	0.65
	DMS	0.430	0.70	0.45	0.50		0.47	0.45
	DMDS	0.866	1.35	0.93		0.95		
2B	H_2S	0.925	0.45	0.50	0.20		0.35	0.25
	MeSH	1.96	1.52	1.50	1.45		1.38	1.23
	DMS	1.93	3.25	2.15	2.60		2.25	1.95
	DMDS	1.38	2.70	1.87		1.80		2.50
3B	H_2S	4.00	3.25	3.15	2.76		3.30	2.46
	MeSH	6.01	5.25	6.00	5.40		5.25	4.45
	DMS	4.76	7.6[b]	6.9[b]	6.8[b]		5.60	4.55
	DMDS	2.83		3.8[b]		3.8[b]		3.25
4B	H_2S	5.84	4.90	4.05	4.55		4.60	3.32
	MeSH	9.99	c	c	c		8.35	6.68
	DMS	7.39	c	6.5[b]	c		9.05[b]	6.90
	DMDS	5.52	c	6.5[b]	c	4.5[b]		4.5[b]

a. Final vendor analysis before shipping.
b. Outside calibration range - values obtained by extrapolation.
c. Outside calibration range.

in the methods owing to the adsorption-desorption phenomenon described above. The correlation coefficients are used to determine if a significant slope exists, which is an indication of a change in the concentration over time. The required correlation coefficients for significance at the 5-percent level are 0.878 and 0.811 for samples of size 5 and 6, respectively.

Significant correlations were obtained for H_2S and COS in cylinder 3A, for COS in cylinder 2A, MeSH in cylinder 2B, and for DMS in cylinder 3B. In cylinder 3A, there was an increase in H_2S concentration from 3.8 to 6.62 ppm, giving an average rate of 0.03 ppm per day. The COS concentration also increased at an average rate (slope) of 0.01 ppm per day, from 3.2 to 4.25 ppm. There was no significant slope on the CS_2 determinations over time, but the scatter in the results indicates that analytical variability would preclude the determination of a trend based upon such a limited amount of data.

The concentration of COS in cylinder 2A decreased at an average rate of 0.004 ppm per day over the course of the study. There was an increasing trend in the H_2S concentration and a decreasing trend in the CS_2 which were not significant.

The decreasing trend for MeSH in cylinder 2B was significant at a rate of 0.002 ppm per day, and H_2S, DMS and DMDS also showed decreased amounts relative to the initial analysis. In the other analyses, however, there was considerable scatter among the points away from the regression line, and correlation was not adequate to say a trend existed. However, the overall impression was that the contents were lower after time. In cylinder 3B, DMS decreased significantly at a rate of 0.02 ppm per day, but all other components could be considered uniform over the time period studied.

No consistent trend appeared among the cylinders for the behavior of the compounds under study. In all four cylinders of mixture A, the concentration of COS at time zero was lower than the vendor analysis, but in two cases it continued to decrease while in one case it increased significantly. Similar behavior was exhibited among analyses for the other two compounds in this mixture. The concentrations in mixture B also behaved erratically, with higher and lower values than the vendor analysis and increasing and decreasing trends. The apparent conclusion is that the concentrations are not verifiable as reported by the vendor, either due to analytical methodology or to changes in concentration with time, and cannot be assumed to be stable upon holding.

DILUTION SYSTEM

A dilution system was constructed as per Section 5.2 of Federal Register 41, pp. 43871, October 4, 1976. Figure 17 is a photograph of the system without the oven top, viewed from above. Not shown is a baffle plate which was mounted near the fan to aid circulation. Results obtained with this system were erratic and were traced to the Komhyr A-150 "constant flow rate" pumps. When dilution air at 1350 mL/min was introduced downstream of the pump, the attendant back pressure caused the pump to leak at its head. The design of the head is such that a leak of this sort is unavoidable. A conversation with the supplier of the A-150 revealed that they were aware of this problem but that the pump was designed to operate against a small constant pressure and not in the system described.

A prototype single-stage dilution system was fabricated which gave consistent dilutions when used in the laboratory analysis of synthetic blends. Flow rates of both the sample gas and the dilution air were regulated by passing each through appropriate lengths of capillary stainless steel tubing while controlling the upstream pressures. The effluents were combined in a stainless steel tubing "tee" leading to 1/4-in Teflon tubing. Possible scavenging effects of the metal parts were tested by analyzing an undiluted blend of low-ppm concentration H_2S and then comparing the results to those obtained while bypassing the dilution system. Within experimental error, no difference was observed. It remains to be determined whether such a simple system could be made to work under field conditions which would require a good filtration device to prevent partial or total plugging of the capillary system.

FIELD STUDIES

Field studies involving Method 16 techniques and equipment were begun in September 1979 by Harmon Engineering & Testing of Auburn, Alabama. Under a separate contract with the QAD, Harmon has been given the responsibility of securing a suitable kraft pulp mill for the testing. Southwest Research Institute is to collaborate in this study to the extent that we will furnish a Tracor Model 560 gas chromatograph equipped with both a Melpar FPD and a Hall Electrolytic Conductivity Detector. This will allow a side-by-side comparison of the two under field conditions. Cylinder gases containing the four TRS compounds will be forwarded to Harmon to facilitate pretest studies and to possibly be used at the kraft mill site. In addition, technical support in the field will be provided.

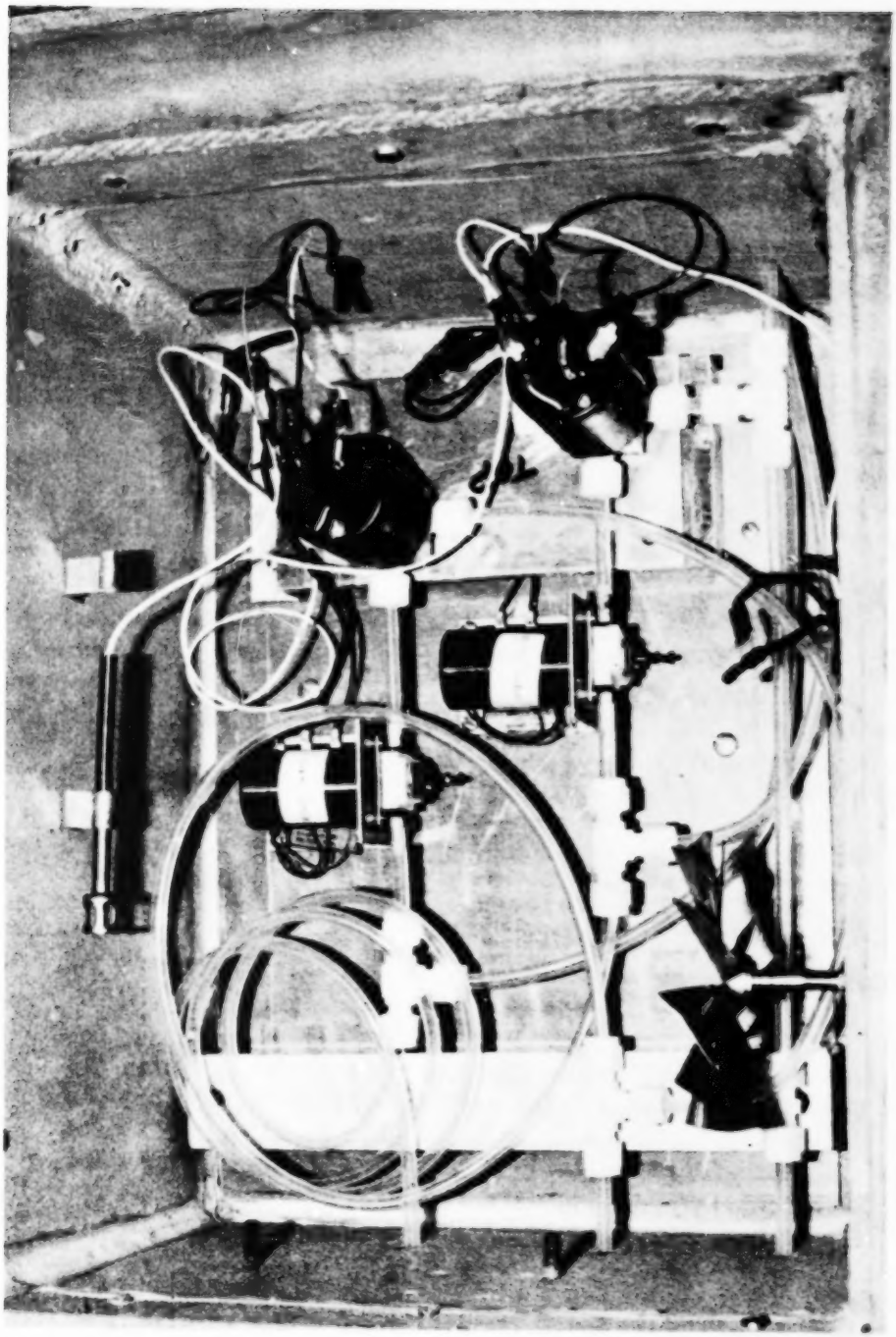

FIGURE 17. TOP VIEW OF OVEN CONTAINING TWO-STAGE DILUTION SYSTEM

REFERENCES

1. A. E. O'Keeffe and G. C. Ortman, Anal. Chem., 38, 760 (1966).

2. F. P. Scaringelli, A. E. O'Keeffe, E. Rosenberg and J. P. Bell, ibid., 42, 871 (1970).

3. W. L. Thornsberry, Jr., ibid., 43, 452 (1971).

4. R. K. Stevens, et al., Environ. Sci. and Technol., 3, 652 (1969).

5. R. K. Stevens and A. E. O'Keeffe, Anal. Chem., 42, 143A (1970).

6. R. E. Pecsar and C. H. Hartman, J. Chromatog. Sci., 11, 492 (1973).

7. S. S. Brody and J. E. Chaney, J. Gas Chromatog., 4, 42 (1966).

8. B. H. Devonald, R. S. Serenius and A. D. McIntyre, Paper presented at the 5th Air and Stream Improvement Conference, Quebec, April 13-15, 1971.

9. R. K. Stevens, A. E. O'Keeffe and G. C. Ortman, Environ. Sci. and Technol., 3, 652 (1969).

10. D. G. Greer and T. J. Bydalek, ibid., 7, 153 (1973).

11. S. O. Farwell and R. A. Rasmussen, J. Chromatog. Sci., 14, 224 (1976).

12. A. Attar, R. Forgey, J. Horn and W. H. Corcoran, ibid., 15, 222 (1977).

13. Dr. Bruce Ferguson, Harmon Engineering Co., Auburn, Alabama, private communication.

14. C. H. Burnett, D. F. Adams and S. O. Farwell, J. Chromatog. Sci., 15, 230 (1977).

15. C. D. Pearson and W. J. Hines, Anal. Chem., 49, 123 (1977).

16. T.L.C. de Souza, D. C. Lane and S. P. Bhatia, Anal. Chem., 47, 543 (1975).

17. T.L.C. de Souza, R. A. Wostradowski, R. Poole, O. Vadas, S. P. Bhatia and S. Prahacs, Pulp and Paper Canada, 79, 242 (1978).

18. Private communication with Jim Nelsen of Bendix Environmental and Process Instruments Division of the Bendix Corporation.

19. A. Jain, Atmospheric Quality Improvement Technical Bulletin No. 81, Appendix F, October 1975.

20. D. L. Williams, "Calibration in Air Monitoring, ASTM STP 598", American Society for Testing and Materials, 183 (1976).

APPENDIX

samples of equal sampling time shall constitute one run. Samples shall be taken at approximately 1-hour intervals.

(d) For the purpose of determining compliance with § 60.104(a)(2), Method 6 shall be used to determine the concentration of SO_2 and Method 15 shall be used to determine the concentration of H_2S and reduced sulfur compounds.

(1) If Method 6 is used, the procedure outlined in paragraph (c)(2) of this section shall be followed except that each run shall span a minimum of four consecutive hours of continuous sampling. A number of separate samples may be taken for each run, provided the total sampling time of these samples adds up to a minimum of four consecutive hours. Where more than one sample is used, the average SO_2 concentration for the run shall be calculated as the time weighted average of the SO_2 concentration for each sample according to the formula:

$$C_r = \sum_{i=1}^{N} C_{s_i} \frac{t_{s_i}}{T}$$

Where:

C_r = SO_2 concentration for the run.
N = Number of samples.
C_{s_i} = SO_2 concentration for sample i.
t_{s_i} = Continuous sampling time of sample i.
T = Total continuous sampling time of all N samples.

(2) If Method 15 is used, each run shall consist of 16 samples taken over a minimum of three hours. The sampling point shall be at the centroid of the cross section of the duct if the cross sectional area is less than 5 m^2 (54 ft^2) or at a point no closer to the walls than 1 m (39 inches) if the cross sectional area is 5 m^2 or more and the centroid is more than 1 meter from the wall. To insure minimum residence time for the sample inside the sample lines, the sampling rate shall be at least 2 liters/minute (0.1 ft/min). The SO_2 equivalent for each run shall be calculated as the arithmetic average of the SO_2 equivalent of each sample during the run. Reference Method 4 shall be used to determine the moisture content of the gases. The sampling point for Method 4 shall be adjacent to the sampling point for Method 15. The sample shall be extracted at a rate proportional to the gas velocity at the sampling point. Each run shall span a minimum of four consecutive hours of continuous sampling. A number of separate samples may be taken for each run provided the total sampling time of these samples adds up to a minimum of four consecutive hours. Where more than one sample is used, the average moisture content for the run shall be calculated as the time weighted average of the moisture content of each sample according to the formula:

$$B_{wr} = \sum_{i=1}^{N} B_{w_i} \left[\frac{t_{s_i}}{T}\right]$$

B_{wr} = Proportion by volume of water vapor in the gas stream for the run.
N = Number of samples.
B_{w_i} = Proportion by volume of water vapor in the gas stream for the sample i.
t_{s_i} = Continuous sampling time for sample i.
T = Total continuous sampling time of all N samples.

(Sec. 114 of the Clean Air Act, as amended (42 U.S.C. 7414)).

APPENDIX A—REFERENCE METHODS

7. Appendix A is amended by adding a new reference method as follows:

METHOD 15. DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE EMISSIONS FROM STATIONARY SOURCES

INTRODUCTION

The method described below uses the principle of gas chromatographic separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent usable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the criteria set below are met.

1. Principle and applicability

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) by gas chromatographic (GC) separation and flame photometric detection (FPD).

1.2 Applicability. This method is applicable for determination of the above sulfur compounds from tail gas control units of sulfur recovery plants.

2. Range and sensitivity

2.1 Range. Coupled with a gas chromtographic system utilizing a 1-milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppm. It may be necessary to dilute gas samples from sulfur recovery plants hundredfold (99:1) resulting in an upper limit of about 1000 ppm for each compound.

2.2 The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppm for a 1 ml sample.

3. Interferences

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effects on the flame photometric detector even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluding CO and CO_2 before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatographs should show agreement within the precision limits of section 4.1.

3.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling line can lead to eventual coating and even blockage of the sample line. This problem can be eliminated along with the moisture problem by heating the sample line.

4. Precision

4.1 Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than ±13 percent from the mean of the three injections.

4.2 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period shall not exceed ±5 percent.

5. Apparatus

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.2 The sample line must be made of Teflon,[1] no greater than 1.3 cm (½ in) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120° C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120° C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert material (e.g. stainless steel or Teflon). It must be heated to 120° C and be capable of approximately a 9:1 dilution of the sample.

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1° C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1° C.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.3.4 Flame Photometric Detector.

5.3.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.3.4.2 Power Supply. Capable of delivering up to 750 volts.

5.3.4.3 Recorder. Compatible with the output voltage range of the electrometer.

[1] Mention of trade names or specific products does not constitute an endorsement by the Environmental Protection Agency.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H_2S, COS, and CS_2.

To demonstrate that adequate resolution has been achieved the tester must submit a chromatograph of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5.1 Calibration System. The calibration system must contain the following components.

5.5.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±1.1° C.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1° C.

6. Reagents

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

6.5 Calibration Gases. Permeation tubes, one each of H_2S, COS, and CS_2, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7. Pretest Procedures

The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested. For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid detergent in water, for example, at each joint. Bubbling indicates the presence of a leak.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8. Calibration

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components, particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within ±0.1°C. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K \times P_r / ML$$

Equation 15-1

where:

C = Concentration of permeant produced in ppm.

P_r = Permeation rate of the tube in µg/min.

M = Molecular weight of the permeant, g/g-mole.

L = Flow rate, l/min, of air over permeant @ 20 C, 760 mm Hg.

K = Gas constant at 20°C and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of analysis system. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards in to the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data.

8.5 Calibration of Dilution System. Generate a know concentration of hydrogen sulfied using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H_2S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of section 4.1 are still applicable.

9. Sampling and Analysis Procedure

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if

the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. Post-Test Procedures

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is unacceptable. Sampling losses of 0–20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in section 8. Only H_2S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. Calculations

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least squares line.

11.2 Calculation of SO_2 Equivalent. SO_2 equivalent will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during the given analysis.

$$SO_2 \text{ equivalent} = \Sigma(H_2S, COS, 2\,CS_2)d \qquad \text{Equation 15-2}$$

where:

SO_2 equivalent = The sum of the concentration of each of the measured compounds (COS, H_2S, CS_2) expressed as sulfur dioxide in ppm.
H_2S = Hydrogen sulfide, ppm.
COS = Carbonyl sulfide, ppm.
CS_2 = Carbon disulfide, ppm.
d = Dilution factor, dimensionless.

11.3 Average SO_2 equivalent will be determined as follows:

$$\text{Average } SO_2 \text{ equivalent} = \frac{\sum_{i=1}^{N} (SO_2 \text{ equiv.})_i}{N(1 - Bwo)} \qquad \text{Equation 15-3}$$

where:

Average SO_2 equivalent = Average SO_2 equivalent in ppm, dry basis.
Average SO_2 equivalent = SO_2 in ppm as determined by Equation 15-2.
N = Number of analyses performed.
Bwo = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases (36 FR 24887).

12. Example System

Described below is a system utilized by EPA in gathering NSPS data. This system does not now reflect all the latest developments in equipment and column technology, but it does represent one system that has been demonstrated to work.

12.1 Apparatus.

12.1.1 Sample System.

12.1.1.1 Probe. Stainless steel tubing, 6.35 mm (¼ in.) outside diameter, packed with glass wool.

12.1.1.2 Sample Line. ¼ inch inside diameter Teflon tubing heated to 120° C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120° C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 15-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120° C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Teflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by combining 150 cc of sample with 1350 cc of clean dry air as shown in Figure 15-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120° C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min. ±1 percent per dilution stage.

12.1.3 Gas Chromatograph.

12.1.3.1 Column—1.83 m (6 ft.) length of Teflon tubing, 2.16 mm (0.085 in.) inside diameter, packed with deactivated silica gel, or equivalent.

12.1.3.2 Sample Valve. Teflon six port gas sampling valve, equipped with a 1 ml sample loop, actuated by compressed air (Figure 15-1).

12.1.3.3 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100° C, constant within ±1° C.

12.1.3.4 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1° C.

12.1.3.5 Flow System. Gas metering system to measure sample flow, hydrogen flow, oxygen flow and nitrogen carrier gas flow.

12.1.3.6 Detector. Flame photometric detector.

12.1.3.7 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-7} amperes full scale.

12.1.3.8 Power Supply. Capable of delivering up to 750 volts.

12.1.3.9 Recorder. Compatible with the output voltage range of the electrometer.

12.1.4 Calibration. Permeation tube system (Figure 15-3).

12.1.4.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.4.2 Mass Flowmeters. Two mass flowmeters in the range 0-3 l/min. and 0–10 l/min. to measure air flow over permeation tubes at ±2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter at least once each year.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30° C within ±0.1° C.

12.2 Reagents.

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at 30.0° C.

12.3 Operating Parameters. The operating parameters for the GC/FPD system are as follows: nitrogen carrier gas flow rate of 100 cc/min, exhaust temperature of 110° C, detector temperature 105° C, oven temperature of 40° C, hydrogen flow rate of 80 cc/minute, oxygen flow rate of 20 cc/minute, and sample flow rate of 80 cc/minute.

12.4 Analysis. The sample valve is actuated for 1 minute in which time an aliquot of diluted sample is injected onto the separation column. The valve is then deactivated for the remainder of analysis cycle in which time the sample loop is refilled and the separation column continues to be foreflushed. The elution time for each compound will be determined during calibration.

13. Bibliography

13.1 O'Keeffe, A. E. and G. C. Ortman. "Primary Standards for Trace Gas Analysis." Anal. Chem. 38:760 (1966).

13.2 Stevens, R. K., A. E. O'Keeffe, and G. C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels." Environmental Science and Technology 3:7 (July, 1969).

13.3 Mulick, J. L., R. K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, Calif. April 6-8, 1971.

13.4 Devonald, R. H., R. S. Serenius, and A. D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." Pulp and Paper Magazine of Canada, 73:3 (March, 1972).

13.5 Grimley, K. W., W. S. Smith, and R. M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis on a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting in St. Louis, Mo. June 14-19, 1970.

13.6 General Reference. Standard Methods of Chemical Analysis Volume III A and B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

[FR Doc. 78-6633 Filed 3-14-78; 8:45 am]

shall be corrected to 8 volume percent oxygen. These corrections shall be made in the manner specified in § 60.284(c)(3).

APPENDIX A—REFERENCE METHODS

(3) Method 16 and Method 17 are added to Appendix A as follows:

* * * * *

METHOD 16. SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

Introduction

The method described below uses the principle of gas chromatographic separation and flame photometric detection. Since there are many systems or sets of operating conditions that represent usable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the criteria set below are met.

1. *Principle and Applicability.*

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are known collectively as total reduced sulfur (TRS).

1.2 Applicability. This method is applicable for determination of TRS compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills.

2. *Range and Sensitivity.*

2.1 Range. Coupled with a gas chromatographic system utilizing a ten milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 1 ppm. This limit is expanded by dilution of the sample gas before analysis. Kraft mill gas samples are normally diluted tenfold (9:1), resulting in an upper limit of about 10 ppm for each compound.

For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size to 1 milliliter.

2.2 Using the sample size, the minimum detectable concentration is approximately 50 ppb.

3. *Interferences.*

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effect on the flame photometric detector even after 9:1 dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatographs should show agreement within the precision limits of Section 4.1.

3.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference must be eliminated by use of a probe filter.

3.4 Sulfur Dioxide. SO_2 is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from other compounds of interest. The procedure must be designed to eliminate this problem either by the choice of separation columns or by removal of SO_2 from the sample.

Compliance with this section can be demonstrated by submitting chromatographs of calibration gases with SO_2 present in the same quantities expected from the emission source to be tested. Acceptable systems shall show baseline separation with the amplifier attenuation set so that the reduced sulfur compound of concern is at least 50 percent of full scale. Base line separation is defined as a return to zero ± percent in the interval between peaks.

4. *Precision and Accuracy.*

4.1 GC/FPD and Dilution System Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than ±3 percent from the mean of the three injections.

4.2 GC/FPD and Dilution System Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period shall not exceed ± percent.

4.3 System Calibration Accuracy. The complete system must quantitatively transport and analyze with an accuracy of 20 percent. A correction factor is developed to adjust calibration accuracy to 100 percent.

5. *Apparatus* (See Figure 16-1).

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.2 Sample Line. The sample line must be made of Teflon,[1] no greater than 1.3 cm (½) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120° C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120° C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert materials (e.g., stainless steel or Teflon). It must be heated to 120° C. and be capable of approximately a 9:1 dilution of the sample.

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1° C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1° C.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

5.3.4 Flame Photometric Detector.

5.3.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.3.4.2 Power Supply. Capable of delivering up to 750 volts.

5.3.4.3 Recorder. Compatible with the output voltage range of the electrometer.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences.

To demonstrate that adequate resolution has been achieved, the tester must submit a chromatograph of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined in Section 3.4. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5. Calibration System. The calibration system must contain the following components.

5.5.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

5.5.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±0.1° C.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1° C.

6. *Reagents.*

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons. This gas must be heated prior to mixing with the sample to avoid water condensation at the point of contact.

6.5 Calibration Gases. Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, agravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7. *Pretest Procedures.* The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. In any component, or if the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8. *Calibration.* Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in Section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires a understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components; particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within ±0.1° C. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of Section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K\frac{P_r}{L}$$

Equation 16-1

where:

C = Concentration of permeant produced in ppm.

P_r = Permeation rate of the tube in μg/min.

M = Molecular weight of the permeant (g/g-mole).

L = Flow rate, l/min, of air over permeant @ 20° C, 760 mm Hg.

K = Gas constant at 20° C and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of analysis system. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in Section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data.

8.5 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in Section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H_2S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of Section 4.1 are still applicable.

9. *Sampling and Analysis Procedure.*

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximtely 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. *Post-Test Procedures.*

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to insure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is unacceptable. Sampling losses of 0-20 percent must be corrected for by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 8. Only H_2S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. *Calculations.*

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least square line.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each anaylsis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$TRS = \Sigma (H_2S, MeSH, DMS, 2DMDS)d$$

Equation 16-2

where:

TRS = Total reduced sulfur in ppm, wet basis.

H_2S = Hydrogen sulfide, ppm.

MeSH = Methyl mercaptan, ppm.

DMS = Dimethyl sulfide, ppm.

DMDS = Dimethyl disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Average TRS} = \frac{\sum_{i=1}^{N} TRS_i}{N\left(1-B_{wo}\right)}$$

Average TRS = Average total reduced sulfur in ppm, dry basis.
TRS_i = Total reduced sulfur in ppm as determined by Equation 16-2.
N = Number of samples.
B_{wo} = Fraction of volume of water vapor in the gas stream as determined by method 4—Determination of Moisture in Stack Gases (36 FR 24887).

11.4 Average concentration of individual reduced sulfur compounds.

$$C = \frac{\sum_{i=1}^{N} S_i}{N}$$

Equation 16-3

where:

S_i = Concentration of any reduced sulfur compound from the ith sample injection, ppm.
C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.
N = Number of injections in any run period.

12. *Example System.* Described below is a system utilized by EPA in gathering NSPS data. This system does not now reflect all the latest developments in equipment and column technology, but it does represent one system that has been demonstrated to work.

12.1 Apparatus.

12.1.1 Sampling System.

12.1.1.1 Probe. Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. the probe is designed with the deflector shield placed between the sample and the gas inlet holes and the glass wool plugs to reduce clogging of the filter and possible adsorption of sample gas. The exposed portion of the probe between the sampling port and the sample line is heated with heating tape.

12.1.1.2 Sample Line ⅜ inch inside diameter Teflon tubing, heated to 120° C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120° C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 16-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120° C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Tcflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by combining 150 cc of sample with 1,350 cc of clean dry air as shown in Figure 16-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120° C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min ±1 percent per dilution stage.

12.1.3 Gas Chromatograph Columns. Two types of columns are used for separation of low and high molecular weight sulfur compounds:

12.1.3.1 Low Molecular Weight Sulfur Compounds Column (GC/FPD-I).

12.1.3.1 Separation Column. 11 m by 2.16 mm (36 ft by 0.085 in) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 5 percent polyphenyl ether and 0.05 percent orthophosphoric acid, or equivalent (see Figure 16-3).

12.1.3.1.2 Stripper or Precolumn. 0.6 m by 2.16 mm (2 ft by 0.085 in) inside diameter Teflon tubing packed as in 5.3.1.

12.1.3.1.3 Sample Valve. Teflon 10-port gas sampling valve, equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.3.1.4 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100° C, constant within ±1° C.

12.1.3.1.5 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1° C.

12.1.3.1.6 Flow System. Gas metering system to measure sample flow, hydrogen flow, and oxygen flow (and nitrogen carrier gas flow).

12.1.3.1.7 Detector. Flame photometric detector.

12.1.3.1.8 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

12.1.3.1.9 Power Supply. Capable of delivering up to 750 volts.

12.1.3.1.10 Recorder. Compatible with the output voltage range of the electrometer.

12.1.3.2 High Molecular Weight Compounds Column (GC/FPD-II).

12.1.3.2.1. Separation Column. 3.05 m by 2.16 mm (10 ft by 0.0885 in) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 10 percent Triton X-305, or equivalent.

12.1.3.2.2 Sample Valve. Teflon 6-port gas sampling valve equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.3.2.3 Other Components. All components same as in 12.1.3.1.4 to 12.1.3.1.10.

12.1.4 Calibration. Permeation tube system (figure 16-4).

12.1.4.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.4.2 Mass Flowmeters. Two mass flowmeters in the range 0-3 l/min. and 0-10 l/min. to measure air flow over permeation tubes at ±2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter, at least once each year.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30° C. within ±0.1° C.

12.2 Reagents

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2. Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in Section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibrated Gases. Permeation tubes gravimetrically calibrated and certified at 30.0° C.

12.3 Operating Parameters.

12.3.1 Low-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system used for low molecular weight compounds are as follows: nitrogen carrier gas flow rate of 50 cc/min, exhaust temperature of 110° C, detector temperature of 105° C, oven temperature of 40° C, hydrogen flow rate of 80 cc/min, oxygen flow rate of 20 cc/min, and sample flow rate between 20 and 80 cc/min.

12.3.2 High-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system for high molecular weight compounds are the same as in 12.3.1 except: oven temperature of 70° C, and nitrogen carrier gas flow of 100 cc/min.

12.4 Analysis Procedure.

12.4.1 Analysis. Aliquots of diluted sample are injected simultaneously into both GC/FPD analyzers for analysis. GC/FPD-I is used to measure the low-molecular weight reduced sulfur compounds. The low molecular weight compounds include hydrogen sulfide, methyl mercaptan, and dimethyl sulfide. GC/FPD-II is used to resolve the high-molecular weight compound. The high-molecular weight compound is dimethyl disulfide.

12.4.1.1 Analysis of Low-Molecular Weight Sulfur Compounds. The sample valve is actuated for 3 minutes in which time an aliquot of diluted sample is injected into the stripper column and analytical column. The valve is then deactivated for approximately 12 minutes in which time, the analytical column continues to be foreflushed, the stripper column is backflushed, and the sample loop is refilled. Monitor the responses. The elution time for each compound will be determined during calibration.

12.4.1.2 Analysis of High-Molecular Weight Sulfur Compounds. The procedure is essentially the same as above except that no stripper column is needed.

13. *Bibliography.*

13.1 O'Keeffe, A. E. and G. C. Ortman. "Primary Standards for Trace Gas Analy-

sis." Analytical Chemical Journal, 38,760 (1966).

13.2 Stevens, R. K., A. E. O'Keeffe, and G. C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part Per Million Levels." Environmental Science and Technology, 3 7 (July, 1969).

13.3 Mullick, J. D., R. K. Stevens and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6-8, 1971.

13.4 Devonald, R. H., R. S. Serenius, and A. D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." Pulp and Paper Magazine of Canada, 73,3 (March, 1972).

13.5 Grumley, K. W., W. S. Smith, and R. M. Martin. "The Use of a Dynamic Dilution System in the Confirmation of Stack Gases for Automated analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting in St. Louis, Mo. June 14-19, 1970.

13.6 General Reference. Standard Methods of Chemical Analysis Volume III A and B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

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[FR Doc. 79-1210 Filed 1-11-79; 8:45 am]

[6560-01-M]

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

[FRL 1012-2]

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Appendix A—Reference Method 16

AGENCY: Environmental Protection Agency.

ACTION: Amendment.

SUMMARY: This action amends Reference Method 16 for determining total reduced sulfur emissions from stationary sources. The amendment corrects several typographical errors and improves the reference method by requiring the use of a scrubber to prevent potential interference from high SO_2 concentrations. These changes assure more accurate measurement of total reduced sulfur (TRS) emissions but do not substantially change the reference method.

SUPPLEMENTARY INFORMATION: On Februrary 23, 1978 (43 FR 7575), Appendix A—Reference Method 16 appeared with several typographical errors or omissions. Subsequent comments noted these and also suggested that the problem of high SO_2 concentrations could be corrected by using a scrubber to remove these high concentrations. This amendment corrects the errors of the original publication and slightly modifies Reference Method 16 by requiring the use of a scrubber to prevent potential interference from high SO_2 concentrations.

Reference Method 16 is the reference method specified for use in determining compliance with the promulgated standards of performance for kraft pulp mills. The data base used to develop the standards for kraft pulp mills has been examined and this additional requirement to use a scrubber to prevent potential interference from high SO_2 concentrations does not require any change to these standards of performance. The data used to develop these standards was not gathered from kraft pulp mills with high SO_2 concentrations; thus, the problem of SO_2 interference was not present in the data base. The use of a scrubber to prevent this potential interference in the future, therefore, is completely consistent with this data base and the promulgated standards.

The increase in the cost of determining compliance with the standards of performance for kraft pulp mills, as a result of this additional requirement to use a scrubber in Reference Method 16, is negligible. At most, this additional requirement could increase the cost of a performance test by about 50 dollars.

Because these corrections and additions to Reference Method 16 are minor in nature, impose no additional substantive requirements, or do not require a change in the promulgated standards of performance for kraft pulp mills, these amendments are promulgated directly.

EFFECTIVE DATE: January 12, 1979.

FOR FURTHER INFORMATION CONTACT:

Don R. Goodwin, Director, Emission Standards and Engineering Division, (MD-13) Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number 919-541-5271.

Dated: January 2, 1979.

DOUGLAS M. COSTLE,
Administrator.

Part 60 of Chapter I, Title 40 of the Code of Federal Regulations is amended as follows:

APPENDIX A—REFERENCE METHODS

In Method 16 of Appendix A, Sections 3.4, 4.1, 4.3, 5, 5.5.2, 6, 8.3, 9.2, 10.3, 11.3, 12.1, 12.1.1.3, 12.1.3.1, 12.1.3.1.2, 12.1.3.2, 12.1.3.2.3, and 12.2 are amended as follows:

1. In subsection 3.4, at the end of the first paragraph, add: "In the example system, SO_2 is removed by a citrate buffer solution prior to GC injection. This scrubber will be used when SO_2 levels are high enough to prevent baseline separation from the reduced sulfur compounds."

2. In subsection 4.1, change "± 3 percent" to "± 5 percent."

3. In subsection 4.3, delete both sentences and replace with the following: "Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent."

4. After Section 5 and before subsection 5.1.1 insert "5.1. Sampling."

5. In Section 5, add the following subsection: "5.3 SO_2 Scrubber. The SO_2 scrubber is a midget impinger packed with glass wool to eliminate entrained mist and charged with potassium citrate-citric acid buffer." Then increase all numbers from 5.3 up to and including 5.5.4 by 0.1, e.g., change 5.3 to 5.4, etc.

6. In subsection 5.5.2, the word "lowest" in the fourth sentence is replaced with "lower."

7. In Section 6, add the following subsection: "6.6 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. 284 grams of sodium citrate may be substituted for the potassium citrate."

8. In subsection 8.3, in the second sentence, after "Bypassing the dilution system," insert "but using the SO_2 scrubber," before finishing the sentence.

9. In subsection 9.2, replace sentence with the following: "Aliquots of diluted sample pass through the SO_2 scrubber, and then are injected into the GC/FPD analyzer for analysis."

10. In subsection 10.3, "paragraph" in the second sentence is corrected with "subsection."

11. In subsection 11.3 under B_{a_2} definition, insert "Reference" before "Method 4."

12. In subsection 12.1.1.3 "(12.2.4 below)" is corrected to "(12.1.2.4 below)."

13. In subsection 12.1, add the following subsection: "12.1.3 SO_2 Scrubber. Midget impinger with 15 ml of potassium citrate buffer to absorb SO_2 in the sample." Then renumber existing section 12.1.3 and following subsections through and including 12.1.4.3 as 12.1.4 through 12.1.5.3.

14. The second subsection listed as "12.1.3.1" (before corrected in above amendment) should be "12.1.4.1.1."

15. In subsection 12.1.3.1 (amended above to 12.1.4.1) correct "GC/FPD-1 to "GC/FPD-I."

16. In subsection 12.1.3.1.2 (amended above to 12.1.4.1.2) omit "Packed as in 5.3.1." and put a period after "tubing."

17. In subsection 12.1.3.2 (amended above to 12.1.4.2) correct "GC/FPD-11" to "GC/FPD-II."

18. In subsection 12.1.3.2.3 (amended above to 12.1.4.2.3) the phrase "12.1.3.1.4. to 12.1.3.1.10" is corrected to read "12.1.4.1.5 to 12.1.4.1.10."

19. In subsection 12.2, add the following subsection: "12.2.7 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. 284 grams of sodium citrate may be substituted for the potassium citrate."

(Sec. 111, 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7601 (a))).

[FR Doc. 79-1047 Filed 1-11-79; 8:45 am]